CONGO RED (CR) REMOVAL FROM AQUEOUS SOLUTION BY COMMERCIAL AND LABORATORY PREPARED LOW COST ADSORBENTS USING ADSORPTION

a thesis submitted in partial fulfillment of the requirements for the degree of

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by

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled *"Congo Red (CR) Removal from Aqueous Solution by Commercial and Laboratory Prepared Low Cost Adsorbents using Adsorption"* in the partial fulfillment of the requirements of the award of the degree of Master of Technology (Res.) in Chemical Engineering, submitted in the Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, is an authentic record of my own work carried out during the period of Feb. 2009 to April 2011 under the supervision of Dr. Arvind Kumar, Assistant Professor, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: Sept. 2011 **(GHANSHYAM BARMAN)**

Place: Rourkela

CERTIFICATE

This is to certify that the thesis of the project entitled, *"Congo Red (CR) Removal from Aqueous Solution by Commercial and Laboratory Prepared Low Cost Adsorbents using Adsorption"* submitted by Ghanshyam Barman (608CH104) in partial fulfillment of the requirements for the award of Master of Technology (Res.) in Chemical Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree.

Date: 26.08.11

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GHANSHYAM BARMAN

ABSTRACT

Release of dyes into the environment from industrial practices is a matter of global concern. Dyes are emitted from industrial plants in the form of aqueous effluents. They are widely used in several industries like textile, dyeing, paper and pulp, tannery, paint industries etc. Dyes are considered an objectionable type of pollutant because they are toxic in nature. Their classification can be done based on their usage, group and solubility.

Various treatment processes used for the removal of dyes include adsorption, microbial degradation, wet air oxidation, etc. Use of commercial and low cost adsorbents is a viable option for dyes removal from aqueous effluents. However, high cost of commercial adsorbents like activated carbon and others, and material losses during their regeneration pose an impediment in the utilization of commercial adsorbents. This has led to a search for cheaper alternative materials as adsorbents such as lignin, bagasse pith, peat, saw dust; coal fly ash; rice husk ash and Bio-fuel extract (BFE), etc.

The present study is therefore, aimed to study the process of adsorption of Congo red (CR) onto powdered and granular-activated carbon (PAC & GAC), and indigenously prepared low-cost adsorbents such as Bagasse fly ash (BFA), Rice husk ash (RHA), coconut Ash (CCA), Fruit juice extract (FJE), BAEL (*Aegle marmelos*) and spent tea (ST) and to find out the possibility of using them as low-cost adsorbents for the removal of dyes in general and CR in particular. This investigation also examines the influence and optimization of various process parameters for their optimal performance such as initial concentration of CR (C_0) contact time (t), temperature (T), and initial pH of dye solution. Batch adsorption experiments for the removal of CR from the aqueous solution by PAC, GAC, BFA, RHA, CCA, FJE, BAEL and ST were performed by using Taguchi design methodology. Factors as such pH, temperature, adsorbent dose and contact time were optimized with the bigger-is-better S/N ratio as quality characteristics and analysis of variance with 25 sets of experiments only. The optimum CR removal experimental conditions are obtained for all the adsorbents used with respect to their maximum uptake capacities in the present work.

Moreover, the adsorbents were also characterized for their valuable adsorbable properties like surface area and point of zero charge.

The exhausted low-cost adsorbents along with the sorbed CR can be separated from the solution (by filtration), dried and used as such or as fire briquettes to recover their energy value. The resulting bottom ash blended with cementations mixture can be used for making building blocks or it may be used to make fire bricks.

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INTRODUCTION

1. INTRODUCTION

1.1 General

Water is a key ingredient for sustaining life on planet earth. It is widely used in various industrial utility. With the growth in population, society, science and technology have exploited water up to a great extent; as a result, there is a acute shortage of safe drinking water as it is being polluted by anthropogenic activities. There are mainly three sectors namely agricultural, industrial and domestic sectors consuming 70, 22 and 8% of available fresh water respectively. (Helmer and Hespanhol, 1997; Lehr et al., 1980; Nemerrow, 1978) this has resulted in the generation of large amounts of wastewater (Helmer and Hespanhol, 1997; Lehr et al., 1980; Nemerrow, 1978) containing a number of 'pollutants'. One of the important class of the pollutants is dyes, once they discharge in to the water receiving bodies creates several environmental problems, such as colour interferes with penetration of sunlight in to water, retards photosynthesis, inhibits growth of aquatic biota and gas solubility in water.

At present there are more than 100,000 commercial dyes and the annual production of these commercial dyes is estimated to be $7x10^5$–$1x10^6$ tons per year (Christie, 2007; Hunger, 2003; Husain, 2006; Meyer, 1981; Zollinger, 1987). It is reported that 10–15% of the used dyes enter the environment through wastes (Hai et al., 2007; Husain, 2006). The main consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities. Dyes are considered an objectionable type of pollutant because they are toxic (Bae and Freeman, 2007; Christie, 2007; Combes and Havelandsmith, 1982; Nemerow and Doby, 1958) generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity (Christie, 2007; Hatch and Maibach,1999; Rai et al., 2005).

Dyes are basically complicated molecules and very difficult to degrade naturally in water system and sometimes may forms carcinogenic products. The presence of basic and azo dyes increases toxicity of water (Forgacs et al., 2004; Rai et al., 2005). Dyes exhibit considerable structural diversity and can be classified in several ways. However, their classification can also be done based on their solubility and insolubility, rate and dispersion (Hunger, 2003) both by their chemical structure and their application to the fiber type: soluble dyes which

include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. Table 1 comprising the classification of dyes based on their usage, group and solubility.

There are several ways and means to remove the dyes from wastewater. For this various methodologies have been presented in Table 2. Adsorption is the most popular physico-chemical treatment for the removal of organic pollutants from wastewaters. The various phenomena pertaining to decolonization and adsorptive efficiencies of adsorbents have been correlated. A number of non-conventional, low cost adsorbents have been tried for dye removal. Use of commercial and low cost adsorbents is a viable option for dyes removal from aqueous effluents. However, high cost of commercial adsorbents like activated carbon and others, and material losses during their regeneration pose an impediment in the utilization of commercial adsorbents. This has led to a search for cheaper alternative materials as adsorbents such as lignin, bagasse pith, peat, saw dust, coal fly ash, rice husk ash and Bio-fuel extract etc.

Batch adsorption experiments for the removal of Congo Red (CR) from the aqueous solution by GAC, PAC, BFA, RHA, CCA, FJE, BAEL **(***Aegle marmelos)* and ST were performed by using Taguchi design methodology.

1.2 Objectives

Following are the objectives of the present study

- Development of cost effective adsorbents for CR removal.
- Characterization of the developed adsorbents for its various valuable properties such as surface area and point of zero charge.
- Estimation of adsorption capacities of the adsorbents over varying concentration of CR
- Process variables optimization using Taguchi experimental design.

Table 1.Classification of dyes based on their usage, group and solubility.

Types of dyes	Uses	Groups	Water Solubility
Acid Dyes	Nylon, Wool,Silk,Modified Acrylics, Paper, Leather, Ink-jet-printing, Food, Cosmetics	Azo(premetallized), Anthraquinone, Triphenylmethane, Azine,Xanthenes,Nitro and Nitroso	Soluble
Cationic (Basic) Dyes	Paper,Polyacrylonitrile,Modified Polyesters,Cation dye able polyethylene terephthalate ,Medicine	Diazahemicyanine,Triarylmethane,Cyanine,Hemicyanine,Thiazine,Oxazine and Acridine	
Disperse Dyes	Polyester, Nylon, Cellulose, Cellulose Acetate, Acrylic fibers	Azo,Anthraquinone, Styryl,Nitro and Benzodifuranone	Insoluble
Direct Dyes	Nylon, Rayon, Paper,Leather,Cotton	Polyazo,Stilbenes,Pthalocyanines and Oxazines	Soluble
Reactive Dyes	Nylon , Paper , Cotton, Cellulose	Azo,Anthraquinone,,Triarylmethane, pthalocyanine ,Oxazine and formazon	_
Solvent Dyes	Plastics,gasoline,lubricants,oils, and waxes	Sulphonic acid, carboxylic acid quaternary ammonium, Azo,Anthraquinone,,Triarylmethane, pthalocyanine	Insoluble
Sulphur Dyes	Cotton,rayon,polyamide fibers Paper, Leather, Silk, wood		
Vat Dyes	Cotton ,soluble leuco salts, Cellulosic fibers, rayon and wool	Anthraquinone (including polycyclic quinones) and indigoids	Insoluble

Table 2. Some of the methodologies lying in above mentioned categories are discussed in brief in subsequent paragraphs.

Methodologies	Basic principles	Options	Drawbacks	Reference
Sedimentation	Gravity settling	_	_	Cheremissinoff, 2002
Filtration	Pressure difference	Microfiltration,ultrafiltration,Nano-filtration and reverse osmosis	High working pressure, high energy consumption, membrane clogging, high cost of membrane, short membrane life.	Avlonitis et al., 2008; Sostar-Turk et al., 2005
Chemical treatment	flocculation	Combination of flocculants/coagulants	Expensive due to cost of chemicals, large sludge production, pH dependant.	Zhou et al., 2008; Lee et al., 2006
Oxidation	wastewater is treated by using oxidizing agents	Chemical oxidation, UV assisted oxidation , Fenton's reagent	Unavoidable side reactions, produces toxic compounds, corrosion in metallic vessels, used for water- insoluble dyes, disperse dye and vat dyes are resistant to discoloration by this process.	Namboodri et al., 1994a,b
H_2O_2	Per-oxidization	_	Sludge production, pH dependant	
Fenton's reagent method	solution of hydrogen peroxide and an iron catalyst is also used to oxidize dye wastewaters	_	disperse dyes and vat dyes are resistant to this process, longer reaction time, effective in narrow pH range(<3.5)	Cheng et al., 2004; Kim et al., 2004; Wang, 2008
Ozonation	used to remove the colour and chemical oxygen demand	_	Effective for textile effluent, Does not minimize COD significantly	Sundrarajan et al., 2007
Electrochemical methodology	electro-degradation of dyes	Electro-oxidisation, electro-coagulation	High electricity cost, sludge production, pollution from chlorinated organics	Faouzi et al., 2007; Gupta and Suhas, 2009
Advanced Oxidation Processes	Degradation of dye accelerated by production of the hydroxyl free radical	includes techniques as Fenton's reagent oxidation, ultra violet (UV) photolysis and Sonolysis	UV process in conjunction with peroxide is used to achieve maximum dye degradation	Namboodri and Walsh (1996)
Photo-Fenton process	combination of Fenton reaction in UV light	_	Effective for low dye concentration	Bandala et al., 2008

Photo catalysis	Electron energized by light(photon) hydroxyl radicals forms having high oxidizing potential and therefore can attack most organic structures causing oxidation	_	Sunlight is essential for considerable discoloration (compared to UV light)	Ghorai et al., 2007
Sonolysis	Ultrasound power	Photolysis with sonification	Ultrasound power, total solution volume	Maezawa et al., 2007;
Aerobic treatment	Degradation of organic compounds by bacteria	_	Recalcitrant to biological breakdown, non transformable under aerobic conditions,	Rai et al., 2005; Husain, 2006
Anaerobic treatment	Degradation of dye compounds	_	Insufficient BOD removal, non-mineralization of dyes, nutrients (N, P) is not removed, sulphates changes to sulphide.	Forgacs et al., 2004; Delee et al., 1998
Combined Aerobic -Anaerobic treatment	anaerobic colorization followed by aerobic post treatment		Low biodegradability of dyes, less flexibility in design and operation, larger land area is requirement, longer time required	Bhattacharyya and Sarma, 2003; Crini, 2006
Adsorption	material is concentrated at a solid surface	Physiosorption, chemisorption	Applicable for low concentration only	Cheremissinoff, 2002
Ion exchange	ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle	_	shares various common features along with adsorption	LeVan et al., 1997

Chapter-2

MATERIALS AND METHOD

2. MATERIAL AND METHOD

2.1 Adsorbent and its preparations

BAEL, CCA, ST, BFA (ash from bio fuel producer) and FJE were obtained locally in the vicinity of Rourkela, Orissa washed with hot water (70 ^{o}C) and dried. The activated carbons (both PAC and GAC) were used as procured. RHA (rice husk ash) was obtained from Vandana Power limited, Bilaspur (Chhattisgarh). The origin of the activated carbons is not known, but being from different manufacturers, they possess different characteristics.

Activated carbon-powder and granular were used without chemical activation. The chemical activation of BFA, RHA and ST were carried out by treating all these three with 0.01 M HCl solution and dried at 105 ^{o}C for 12h. To remove the residual acid that was left in BFA, RHA and ST were soaked in 3% $NaHCO_3$. Finally the adsorbents were dried at 105 ^{o}C for 12 h and cool in the desiccators for further use. BFA, CCA and FJE were obtained from the local market of Rourkela city. They were shredded using ball mill and sieved for obtaining the particular granular size. Similar procedure was followed for chemical activation to BF, CSA and FJE as used for BFA, RHA and ST. The dried materials were calcined in a muffle furnace starting from room temperature to 500 ^{o}C (time period of 4.5h) and then washed with DDW two or three times till the ash contents were removed. To obtain end use adsorbents, the procedure was followed as for BFA, RHA and ST.

2.2 Adsorbents characterization

The specific surface area of all the adsorbents were carried out at Kunash Instruments Pvt. Ltd., Mumbai, by N_2 adsorption using Micromeritics instrument (Tristar 3000) and by using Brunauer–Emmett–Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15 K).

The zero surface charge characteristics of all the prepared adsorbents for CR removal were determined by using the solid addition method [Kumar et al. 2008]. Forty milliliters of 0.1M KNO_3 solution was transferred to a series of 100 ml stoppered conical flasks. The pH_o values of the solutions were roughly adjusted between 2 and 12 by adding either 0.1N HCl or NaOH. The total volume of the solution in each flask was adjusted exactly to 50 ml by adding

the KNO_3 solution of the same strength. The pHo of the solutions were then accurately noted. One gram of each sample was added to each flask, and the flasks were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($pH=pH_o - pH_f$) was plotted against the pHo. The point of intersection of the resulting curve with abscissa, at which pH=0, gave the pH_{PZC}. This procedure was repeated for different concentrations of KNO_3 for all the samples.

2. 3 Adsorbate

Congo red was used for the preparation of synthetic aqueous solution of Congo red of varying concentration C_o =10-500 mg/l. The required quantity of the adsorbate was accurately weighed and dissolved in a small amount of double distilled water (DDW) and subsequently made up to 1l in a measuring flask by adding DDW. Fresh stock solution as required was prepared every day and was kept at ambient conditions in a glass stoppered glass container. The C_o was ascertained before the start of each experimental run. pH of the different concentration solutions were adjusted using 0.1 M HCl or NaOH. All the used chemicals were of Analytical grade.

The pH of the aqueous solution was an important controlling parameter in the adsorption process of CR dyes. The impact of the pH on the adsorption capacity is likely to be controlled by the properties of the adsorbate and adsorbent. The initial pH of the dye solution was investigated over a range from 2-10.In experiments it was found that an uptake of CR dye increased with decrease in solution pH for PAC, BFA, RHA, ST, FJE and BAEL, whereas it decreases for CCA and GAC with increase in solution pH. The effect of pH in adsorption process can be explained by the fact that the pH of the dye solution can significantly affect the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The reduction of dye adsorption over the pH range may relate to two possible mechanisms: electrostatic interaction and chemical reaction between adsorbents and dyes. The maximum uptake level was observed at lower pH for 6 adsorbents. It is well known that at acidic pH, the negative charge of adsorbent is counterbalanced by H^+ ions hence reducing hindrance to diffusion of dye ions i.e. more protons will be available to protonate the adsorbent surface, thereby increasing the electrostatic attractions between the negatively charged dye anions and positively charged adsorption sites

and causing an increase in the dye adsorption. On the other hand as the pH of the system increases, the number of positively charged ions goes down and the number of negatively charged ions increases this could be due to the reason that at higher pH values, excess OH^- ions compete with dye ions for adsorption sites on the adsorbent surface resulting in less adsorption. A similar behavior was observed for all the eight systems.

2.4 Batch Experimental Program

For each experiment, 50 ml of CR solution of known C_o and a known amount of the adsorbent was taken in a 100 ml air-tight conical flask with a glass stopper. This mixture was agitated in a temperature-controlled shaking water bath at a constant shaking speed of 250 rpm. The uptake q_t (mg/g) of dye at any time, t was calculated as:

$$q_t = \left(\frac{C_o - C_t}{w} \right) V \qquad (1)$$

Where, C_0 is the initial adsorbate concentration (mg/l), V the volume of the wastewaters in the flask (L), C_t the adsorbate (CR) concentration (mg/l) after time t, and w the mass of the adsorbent (g) used in the experiment.

2.5 Analytical Measurements

The concentration of CR in the aqueous solution was determined by using Spectrophotometer operating in the visible range on absorbance mode. Absorbance values were recorded at the corresponding maximum absorbance wavelength λ_{max}=497nm.The calibration curve of the peak area versus CR concentration was used for the determination of the unknown concentration of CR from a sample. Wherever needed, the samples were appropriately diluted to have the CR concentration in the calibration range.

2.6 Taguchi method

Taguchi method uses the signal/noise (S/N) ratio to measure the quality characteristic deviating from the desired value and analysis of variance (ANOVA) are used as the tools of analysis. The experimental conditions having the maximum S/N ratio is considered as the optimal condition and the variability characteristics are inversely proportional to the S/N ratio [Farzaneh et al., 2010].

Taguchi design can determine the effect of factors on characteristic properties and the optimal conditions of the factors. This method is a simple and systematic approach to optimize design for performance, quality, and cost [Cox and Reid, 2000]. In Taguchi approach, orthogonal arrays and analysis of variance (ANOVA) are used as the tools of analysis. ANOVA estimates the effect of a factor on the characteristic properties and experiment can be performed with the minimum replication using the orthogonal arrays [Roy, 1990]. Conventional statistical experimental design can determine the optimal condition on the basis of the measured values of the characteristic properties while Taguchi method can determine the experimental conditions with the least variability as the optimal condition. Taguchi method uses the signal/noise (S/N) ratio to measure the quality characteristic deviating from the desired value. The experimental conditions having the maximum S/N ratio is considered as the optimal condition and the variability characteristics are inversely proportional to the S/N ratio [Park, 1996]

2.7 Design of experiment

Four process variables were selected as controlling factors namely CR concentration, pH, temperature and time. Each factor varied in five levels based on the Taguchi method and an orthogonal array (OA) was employed to reduce the number of experiments for determining the optimal removal process parameters. L_{25} OA which has 25 rows corresponding to the number of tests with four columns at five levels was chosen. Table 5 lists the OA with the design factors and their levels. The response variables for accomplishing this study were CR uptake onto PAC, GAC, BFA, RHA, CCA, FJE, BAEL and ST. The parameters were optimized with the objective to maximizing the uptake of CR using commercial (PAC & GAC) and laboratory prepared low cost adsorbents (BFA, RHA, CCA, FJE, BAEL and ST).

2.8 Model fitting and statistical analysis

The experimental data were analyzed using the statistical software, Minitab 13.4 for the evaluation of the statistical significance of the experimental result.

Chapter-3

LITERATURE SURVEY

LITERATURE REVIEW

Chong et al. (2009) utilized design of experiment, and statistical and modeling tools to understand and optimize photo degradation performance of an annular slurry photo reactor (ASP) system using a newly developed titania impregnated kaolinite photocatalyst (TiO_2-K) for the degradation of Congo Red (CR). Using a Taguchi orthogonal array of L_9 (3^4), only 9 experiments were required, instead of 81 experiments in a conventional one-factor-at-a-time approach, to optimize the operational factors of TiO_2-K loading, pH, aeration rate and CR concentration, and to determine their synergistic factor interactions in the ASP system.

Grabowska and Gryglewicz, (2007) investigated the adsorption of Congo red dye (CR) onto bituminous coal-based mesoporous activated carbon (AC) from aqueous solutions was studied. The ACs used differed significantly in terms of total surface area, pore volume distribution and surface charge properties. The adsorption tests were performed under static conditions at solution pH 7.8-8.3. The pH at the point of zero charge (pH_{PZC}) for ACs used was over 10.

Wang and Wang (2007) conducted a series of biopolymer chitosan/montmorillonite (CTS/MMT) nanocomposites were prepared by controlling the molar ratio of chitosan (CTS) and montmorillonite (MMT). The nanocomposites were characterized by FTIR and XRD. The effects of different molar ratios of CTS and MMT, initial pH value of the dye solution and temperature on adsorption capacities of samples for Congo Red (CR) dye have been investigated. The adsorption capacities of CTS, MMT and CTS/MMT nanocomposite with CTS to MMT molar ratio of 5:1 for CR were compared. The results indicated that the adsorption capacity of CTS/MMT nanocomposite was higher than the mean values of those of CTS and MMT. Therefore, the nanocomposite can be effectively used as an adsorbent for the removal of CR from wastewaters.

Chatterjee et al. (2010) studied the adsorption performance of chitosan (CS) hydrogel beads was investigated after multiwall carbon nanotubes (MWCNTs) impregnation for the removal of Congo-red (CR) as an anionic dye. The study of the adsorption capacity of CS/CNT beads as a

function of the CNT concentration indicated that 0.01% CNT impregnation was the most useful for enhancing the adsorption capacity. The maximum adsorption capacity of CS/CNT beads obtained from the Langmuir model was 450.4 mg/g.

Acemioglu et al. (2004) performed the studied on the adsorption of Congo red from solution was carried out using calcium-rich fly ash with different contact times, concentrations, temperatures, and pHs. While the amount of dye adsorbed per unit weight of fly ash increases with increasing concentration and temperature, it decreases slightly with increasing pH . The adsorption was between 93 and 98% under the conditions studied.

Lian et al. (2009) investigated the ability of Ca-bentonite to remove Congo red dye from aqueous solutions has been carried out as a function of contact time, temperature (20–50^{0}C), pH (5–10) and concentration (50–200 mg /L). An amount of 0.2 g of Ca-bentonite could remove more than 90.0% of the dye from 100 mg/L Congo red dye solution for the temperature range studied here. The amount of dye adsorbed per unit weight of Ca-bentonite increased from 23.25 to 85.29mg/g with increasing concentration from 50 to 200 mg/L, but it had a little change with temperature and decreased slightly with increasing pH.

N, O-carboxymethyl-chitosans (N, O-CMC) with different degree of substitution (DS) were synthesized under heterogeneous conditions by controlling the reaction temperature. The factors influencing adsorption capacity of N,O-CMC such as the DS of N,OCMC, initial pH value of the dye solution and adsorption temperature for anionic dye Congo red (CR) were investigated. Compared with chitosan (78.90 mg/g), N,O-CMC with the DS of 0.35 exhibited much higher adsorption capacity (330.62 mg/g) for CR at the same adsorption conditions. The results in this study indicated that N, O-CMC was an attractive candidate for removing CR from the dye wastewater Wang and Wang (2008).

Bhattacharyya and Sharma, (2004) presented in their work use of leaves of Azadirachta indica (locally known as the Neem tree) in the form of a powder were investigated as a biosorbent of dyes taking aqueous Congo red solution as a model system. The sorbent was made from mature

Neem leaves and was investigated in a batch reactor under variable system parameters such as concentration of the aqueous dye solution, agitation time, adsorbent amount, pH, and temperature. An amount of 0.6 g of the Neem leaf powder (NLP) per litre could remove 52.0–99.0% of the dye from an aqueous solution of concentration 2.87 $\times 10^{-2}$ mmol/l with the agitation time increasing from 60 to 300 min. The results point to the effectiveness of the Neem leaf powder as a biosorbent for removing dyes like Congo red from water.

Chatterjee et al. (2007) Adsorption of Congo red, an anionic azo dye by chitosan hydro beads has been carried out. Adsorption process has been found to be dependent on temperature with optimum activity at 30 ^{o}C. Chitosan beads is a good adsorbent for the removal of Congo red from its aqueous solution and 1 g of chitosan in the form of hydro beads can remove ~ 93 mg of the dye at natural pH (6.0). Adsorption process is dependent on pH and temperature.

Afkhami and Moosavi, (2010) the adsorption of Congo red (CR) onto maghemite nanoparticles (γ-Fe_2O_3) and its desorption was investigated. The adsorption capacity was evaluated using both the Langmuir and Freundlich adsorption isotherm models. Adsorption capacities of CR compared to many other adsorbents and would be a good method to increase adsorption efficiency for the removal of CR in a wastewater treatment process. The maximum adsorption occurred at pH 5.9. The Langmuir adsorption capacity (q_{max}) was found to be 208.33 mg/g of the adsorbent.

Mittal et al. (2009) The present investigation assesses the applicability of waste materials-bottom ash and deoiled soya-for the removal of the colorant Congo red from wastewaters. The adsorption characteristics and dye removal efficiency of adsorbents have been determined by investigating factors such as effect of pH, effect of concentration of the dye, amount of adsorbents, contact time, and temperature. Column operations depicted good adsorptive tendencies for Congo red with 96.95% and 97.14% saturation of dye on bottom ash and deoiled soya, respectively. Regeneration of the saturated columns has been made by eluting NaOH solution and more than 90% dye has been recovered in both cases.

Yavuz et al. (2002) Monosize and non-porous poly (2-hydroxyethylmethacrylate-co-methylmethacrylate) (poly (HEMA-co-MMA)), microspheres were prepared by dispersion polymerization of HEMA and MMA in an ethanol–water medium in the presence of an initiator (α,α'-azobisisobutyronitrile, AIBN). An affinity dye, i.e. Congo Red (CR) was attached covalently and then Fe3+ ions were incorporated. The poly (HEMA-co- MMA)-CR attached and poly(HEMA-co-MMA)-CR Fe^{3+} incorporated microspheres were used in the immobilization of glucose oxidize (GOD) via adsorption. The adsorption capacities of these microspheres were determined by varying the concentration of GOD in the adsorption medium. GOD adsorption capacities of the Fe^{3+} incorporated microspheres (165 mg/g) were greater than that of the dye-attached microspheres (126 mg/g). Optimum reaction pH was 5.0 for free and 7.0 for both immobilized preparations. Optimum reaction temperature of the adsorbed enzymes was 10◦C higher than that of the free enzyme and was significantly broader. After 10 successive uses the retained activity of the adsorbed enzyme was 93%. It was observed that enzyme could be repeatedly adsorbed and desorbed on the CR attached poly (HEMA-co-MMA) microspheres without significant loss in adsorption capacity or enzyme activity.

Sudipta Chatterjee et al (2008) studied the adsorption of Congo red (CR) onto chitosan (CS) beads impregnated by a cationic surfactant (CTAB, cetyl trimethyl ammonium bromide) was investigated. Chitosan beads impregnated at a ratio of 1/20 of CTAB to CS (0.05% of CTAB and 1% of CS) increased the CR adsorption capacity by 2.2 times from 162.3 mg/g (0% CTAB) to 352.5 mg/g (0.05% CTAB). The CR adsorption decreased with an increase in pH of the CR solution from 4.0 to 9.0 the impregnation of CS beads by cationic surfactants showed the highest adsorption capacities of CR compared to any other adsorbents.

Bulut et al. (2008) conducted the adsorption of CR from aqueous solutions onto bentonite in the concentration range 75–300 mg/L at pH 6.8 and 298 K. The adsorbed amounts of CR increased with increase in contact time and reached the equilibrium after 60 min. The equilibrium time is independent of initial CR concentration and concluded that bentonite has considerable potential for the removal of CR from aqueous solution over a wide range of concentration. It may further

be concluded that bentonite may be used as a low-cost, natural and abundant source for the removal of CR and they may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species such as heavy metals, dyes and other hazardous pollutants, present in the waste effluents.

Panda et al. (2009) Jute stick powder (JSP) has been found to be a promising material for adsorptive removal of Congo red (C.I. 22120) and Rhodamine B (C.I. 45170) from aqueous solutions. Physico-chemical parameters like dye concentration, solution pH, temperature and contact time have been varied to study the adsorption phenomenon. Favorable adsorption occurs at around pH 7.0 whereas temperature has no significant effect on adsorption of both the dyes. The maximum adsorption capacity has been calculated to be 35.7 and 87.7 mg/g of the biomass for Congo red and rhodamine B, respectively.

Tor and Cengeloglu, (2006) studied the effects of contact time; pH, adsorbent dosage and initial dye concentration on the adsorption were investigated. The pH of the dye solution strongly affected the chemistry of both the dye molecules and activated red mud in an aqueous solution. The effective pH was 7.0 for adsorption on activated red mud. It was found that the sufficient time to attain equilibrium was 90 min.

Pavan et al. (2008) shows that the hybrid anilinepropyl silica xerogel can be used as an effective adsorbent for removing Congo red from aqueous solution. The best pH values for favorable dye adsorption were between 5.0 and 7.0. The dye adsorption equilibrium was attained after 20 min and the maximum adsorption capacity obtained was 22.62 mg of dye per gram of hybrid xerogel.

Namasivayam and Kavitha (2002) the adsorption of Congo red by coir pith carbon was carried out by varying the parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature. The adsorption capacity was found to be 6.7 mg/g of the adsorbent. Acidic pH was favorable for the adsorption of Congo Red.

Purkait et al. (2007) studied the Congo red adsorption onto activated carbon in batch mode. The effects of various operating conditions, like, pH, initial dye concentration, temperature, etc., are investigated. More than 85% adsorption is observed to take place within 5 min for the initial concentration of 50 mg/L. It is found that adsorption is ~100% for the initial dye concentrations of 50–200 mg/L at pH 2. The percentage adsorption decreases to 87, 63 and 25% for the initial dye concentrations of 50, 100 and 200 mg/L, respectively, at the end of the experiment when the pH is 12.

Lian et al. (2009) $CaCl_2$ modified bentonite (BCa^{2+}), a clean and cost-effective adsorbent was prepared for the removal of Congo red dye from water. It was effective for the removal of Congo red with a high adsorption capacity, and the adsorption was favored over a broad pH range (5–10). BCa^{2+} showed higher sorption capacity compared with other common materials used as adsorbents for Congo red dye. The results showed that BCa^{2+}could be employed as a low-cost material for the removal of Congo red from aqueous solutions and adsorption capacity was found to be 227.27 mg/g.

Table 3 and 4 comprising the adsorption capacities of some of the adsorbents and surface areas available in literature.

Table 3. Adsorption capacities of some adsorbents in literature.

	Adsorbent	Adsorption capacity (mg/g)	model	References
1	Chitosan hydrogel beads (CSB)generated by sodium dodecyl sulfate (SDS) and chitosan hydrogel beads (CB) formed by alkali gelation	208.3 and 200.0	Sips model	Chatterjee et al. 2010
2	Active manganese oxide	38.6	Langmuir	Chakrabarti et al. 2009
3	Chitosan grafted poly(butyl methacrylate) (ChgPBMA)	96.7		Konagantia et al.2010
4	CS/CNT hydrogel beads	450.4	Langmuir	Chatterjee et al. 2010
5	Ca-bentonite	23.25 to 85.29		Lian et al. 2009
6.	Organo-attapulgite	189.39	Langmuir	Chen and Zhao, 2009
7	Maghemite nanoparticles	208.33	Langmuir	Afkhami and Moosavi,2010
8	Waste materials—bottom ash and deoiled soya	96.95% and 97.14%		Mittal et al. 2009
9	Wheat bran and rice bran	22.73 and 14.63	Langmuir	Wang and Chen, 2009
10	CS beads impregnated with triton X-100	378.79	Sips model	Chatterjee et al. 2009
	CS beads with sodium dodecyl sulfate	318.47	Sips isotherm	-do-
11	Chitosan (CS) beads and Chitosan beads impregnated at a ratio of 1/20 of CTAB to CS	162.3 and 352.5	Sips isotherm	Chatterjee et al. 2009
12	CS hydrogel beads and CS/CNT hydrogel beads	178.32 and 423.34 (1000mg/l)		Chatterjee et al. 2009
13	A mixed adsorbent with natural clay materials and lime	>94%		Vimonses et al.2010
14	Jute stick powder (JSP)	35.7	Langmuir	Panda et al. 2009
15	Sodium bentonite, kaolin and zeolite	19.9, 5.6 and 4.3		Vimonses et al.2009
16	Semiconductor single-crystalline polar nio(111) nanosheets and conventionally	35.15 and 13.2		Song et al.2009

	prepared nickel oxide powder (CP-nio)			
17	Citrus limonum (lemon) peel	34.5	Langmuir	Bhatnagar et al.2009
18	Cattail root	38.79		Hu et al.2010
19	Porphyra yezoensis Ueda (red alga)	71.46	Langmuir	Wang et al.2009
20	Rice husk ash	98.835%		Choudhury et al.2009
21	Cacl2 modified bentonite	227.27	Langmuir	Lian et al.2009
22	Clay mixtures of different clay minerals, bentonite, kaolin and Zeolite	>95%		Vimonses et al. 2009
23	Acid mine drainage (AMD) sludge	389.1	Langmuir	Wei and Viadero, 2007
24	Reactive fibrous adsorbent prepared through the grafting of 4-vinyl pyridine Monomer onto poly(ethylene terephthalate) (pet) fibers	17.3	Langmuir	Arslan and Yigitoglu, 2008
25	*N*,*O*-carboxymethyl-chitosan/montmorillonite (*N*,*O*-CMC–MMT) nanocomposites	74.24	Langmuir	Wang and Wang, 2008a
26	Coal-based mesoporous activated carbons Kja/Ti, Kja/S/Cafe, Kja/N/Cafe, Sa/N/Cafe	52,159,161, 189	Langmuir	Grabowska and Gryglewicz, 2007
27	CTS, MMT and CTS/MMT nanocomposite	81.23, 12.70, 54.52	Langmuir	Wang and Wang, 2007
28	Nitric acid treated rice husk	26.98	Langmuir	Ponnuasmi et al. 2008
29	N,O-carboxymethyl-chitosans (N,O-CMC) with different degree of substitution (DS) and chitosan (CTS)	330.62 and 78.90	Langmuir	Wang and Wang, 2008c
30	Surfactant-modified montmorillonites (MMT) Octyltrimethylammonium bromide (OTAB), dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB) and stearyltrimethylammonium bromide (STAB)	31.1, 83.6, 229 and 127	Langmuir	Wang and Wang, 2008b
31	Chitosan hydro beads	93	Langmuir	Chatterjee et al. 2007
32	Electro coagulated metals hydroxide sludge (EMHS)	513	Langmuir	Golder et al. 2006

33	Bentonite	158.7	Langmuir	Bulut and Ozacar, 2008
34	Kluyveromyces fragilis cells	49.71	Langmuir	Safarik et al. 2007
35	Open burnt clay	> 98 %		Mumin et al. 2007
36	Low cost activated carbon	21.17	Langmuir	Arivoli et al. 2008
37	Acid activated red mud	7.08	Langmuir	Tor and Cengeloglu, 2006
38	Anilinepropylsilica xerogel	22.62	Langmuir	Pavan et al. 2008
39	Chitosan/organomontmorillonite Nanocomposites [OMMT and CTS/OMMT]	192.4 and 290.8	Langmuir	Wang and Wang, 2007
40	Magnetic solphonated lignite	115-230	Langmuir	Ma and Li, 2006
41	β-CD polymer	36.20	Langmuir	Ozmen and Yilmaz, (2007)
42	Calcium-rich fly ash	93-98%		Acemioglu, 2004
43	Activated carbon prepared from olive stones(OSAC)	167	Langmuir	Souissi, 2005
44	Fly ash	4.125	Langmuir	Rao and Rao, 2006
45	Azadirachta indica (Neem tree)	41.2–28.3	Langmuir	Bhattacharyya and Sharma 2004
46	Fertilizer plant waste carbon (WC)	233.86	Langmuir	Mall et al. 2005
47	Carbon slurry waste	272	Langmuir	Bhatnagar et al. 2005
48	Jute processing waste (JPW)	13.18	Langmuir	Banerjee and Dastidar, 2005
49	Azadirachta indica (Neem)	72.38	Langmuir	Sharma and Bhattacharyya. 2005
50	Fungal biomass (A. Niger) and Fungal biomass (A. Niger) Pretreated by $NaHCO_3$	12.10 and 14.72		Fu and Viraraghavan, 2002

51	Waste red mud	4.05	Namasivayam and Arasi, 2005
52	Coir pith carbon	6.7	Namasivayam and Kavitha, 2002

Table 4. Adsorbents and their surface area

Material	**Surface area of adsorbent(m^2/g)**	**Source**
GAC	462.67	Present study
BEL	391.35	Present study
RHA	24.28	Present study
BFE	17.38	Present study
FJE	109	Present study
PAC	1196.85	Present study
CSC	431.72	Present study
GAC Filtrasorb 400(Chemviron Carbon UK)	1100	Ozacar and Sengil(2002)
Filtrasorb F 400	$(1.05–1.2)\times10^6$ m^2/kg	Choy et al. (2000)
PAC Chemviron GW	1026	Martin et al. (2003)
Fly ash-Czech Republic	5.47	Janos et al. (2003)
AC Rice husk	352	Mohamed (2004)
Carbonaceous adsorbent	380	Jain et al. (2003c)
Blast furnace sludge	28	Jain et al. (2003c)
DTMA-bentonite	767	Ozcan et al. (2004a)
Modified silica	187	Phan et al. (2000)
AC-Corncob	943	Juang et al. (2002)
AC-Bagasse	607	Juang et al. (2002)
AC-Plum kernel	1162	Juang et al. (2002)
Cane (bagasse) pith	606.8	Juang et al. (2002)
Wood	3.8–6.4	Poots et al. (1976b)
AC-Pinewood	902	Tseng et al. (2003
Calcined alunite	42.8	Ozacar and Sengil(2002)
Activated sewage sludge	390	Otero et al. (2003b)
Pyrolysed sewage sludge	80	Otero et al. (2003b)

AC-Bagasse	1433	Valix et al. (2004)
Soy meal hull	0.7623	Arami et al. (2006)
AC sludge based	253	Martin et al. (2003)
AC-Sugarcane bagasse	790	Tsai et al. (2001)
Banana peel	20.6–23.5	Annadurai et al.(2002)
Orange peel	20.6–23.5	Annadurai et al.(2002)
AC from gingelly seed shell	229.65	Thinakaran et al.(2008)
AC from cotton seed shell	124.35	Thinakaran et al.(2008)
AC from pongam seed shell	324.79	Thinakaran et al.(2008)
Soy meal hull	0.7623	Arami et al. (2006)
Coir pith carbonized	259	Namasivayam et al.(2001b)
Fly ash-Czech Republic	5.47	Janos et al. (2003)
Calcined alunite	42.8	Ozacar and Sengil(2002)
Sawdust carbon	516.3	Malik (2003)
Rice husk carbon	272.5	Malik (2003)
Carbonaceous adsorbent	380	Jain et al. (2003c)
Blast furnace sludge	28	Jain et al. (2003c)
CAC granular Wako (Wako pure chemicals)	1150	Okada et al. (2003)
CAC fiber FE400 (Toho Rayon Co.)	1010	Okada et al. (2003)
CAC felt KF1500 (Toyobo Co.)	1480	Okada et al. (2003)
CAC Merck	765	Malik et al. (2007)
PAC Chemviron GW	1026	Martin et al. (2003)
Carbonaceous adsorbent	380	Jain et al. (2003b)
Blast furnace (BF) sludge, BF dust, BF slag	28, 13, 4	Jain et al. (2003b)
AC-Pinewood	902	Tseng et al. (2003)
AC-Waste newspaper	1740	Okada et al. (2003)
Bentonite	28	Ozacar and Sengil (2006)

AC-Apricot shell	783	Aygun et al. (2003)
AC-Hazelnut shell	793	Aygun et al. (2003)
AC-Walnut shell	774	Aygun et al. (2003)
Fly ash-Slovakia	3.26	Janos et al. (2003)
Banana peel (raw)	20.6–23.5	Annadurai et al. (2002)
Orange peel (raw)	20.6–23.5	Annadurai et al. (2002)
Clay	71	Bagane and Guiza (2000)
Diatomite	27.8	Al-Ghouti et al. (2003)
Diatomite	33	Shawabkeh and Tutunji (2003)
Clay	30	Gurses et al. (2004)
Yellow passion fruit	30	Pavan et al. (2008)
Beer brewery waste	4.5	Tsai et al. (2008)
Carbonaceous adsorbent	380	Jain et al. (2003a)
Fly ash (treated with H_2SO_4)	6.236	Lin et al. (2008)
Fly ash, zeolite, unburned carbon	15.6, 16.0,224	Wang et al. (2005b)
Sunflower stalk	1.2054	Sun and Xu (1997)
AC from pine sawdust	1390	Akmil-Basar et al. (2005)
AC-groundnut shell	1114	Malik et al. (2007)
Carbonaceous material	629	Gupta et al. (1997)
Carbonaceous adsorbent	380	Jain et al. (2003b)
Bentonite	47.73	Hu et al. (2006a)
AC-Bagasse	607	Juang et al. (2002)
Cane pith	606.8	Juang et al. (2001)
AC-Corncob	943	Juang et al. (2002)
AC sludge based	253	Martin et al. (2003)
Coir pith carbonized	259	Namasivayam et al. (2001a)
Activated sewage sludge	390	Otero et al. (2003b)

Pyrolysed sewage sludge	80	Otero et al. (2003b)
PAC Chemviron GW	1026	Martin et al. (2003)
Rice hull ash	236.4	Chou et al. (2001)
Sunflower stalk	1.2054	Sun and Xu (1997)
Crude sewage sludge	5.28	Dhaouadi and M'Henni (2008)
Mixture almond shells	10.5	Doulati Ardejani et al.(2008)
Soy meal hull	0.7623	Arami et al. (2006)
AC from biomass Euphorbia rigida	741–21	Gercel et al. (2008)
Modified sepiolite	50.5	Ozdemir et al. (2004)
Modified zeolite	11.8	Ozdemir et al. (2004)
High lime fly ash	5.35	Eren and Acar (2007)
Calcined alunite	66	Ozacar and Sengil(2003)

Chapter-4

RESULT AND DISCUSSION

4 RESULT AND DISCUSSION

The objective of experiment is to optimize parameters to get higher uptake of CR onto commercial and low cost adsorbents; the higher the better characteristics were used. Table 5 shows the actual data for CR uptake with computed S/N ratio. Whereas Table 6 show the mean S/N ratio for each levels of CR uptake. These data were then plotted through Figs. 1-8.

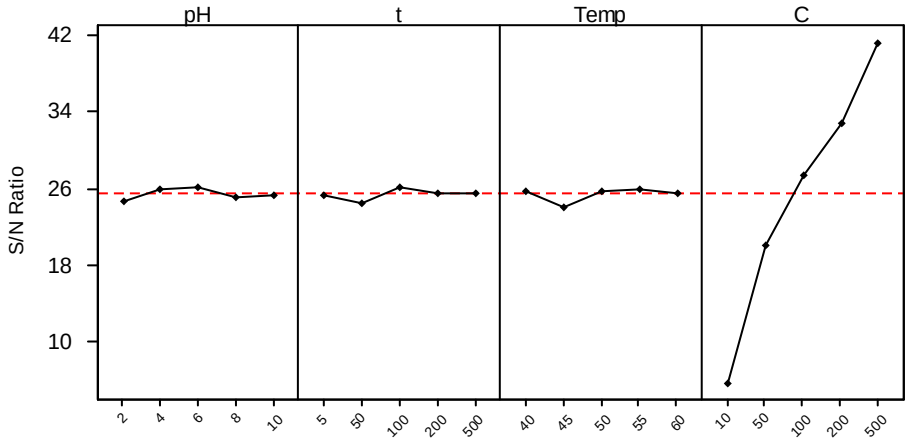

Fig. 1 The higher the better S/N graph for CR uptake onto PAC

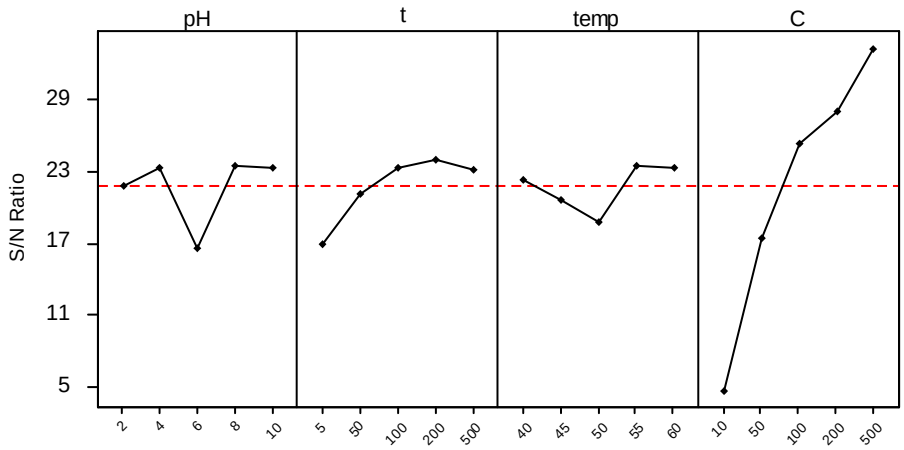

Fig. 2 The higher the better S/N graph for CR uptake onto GAC

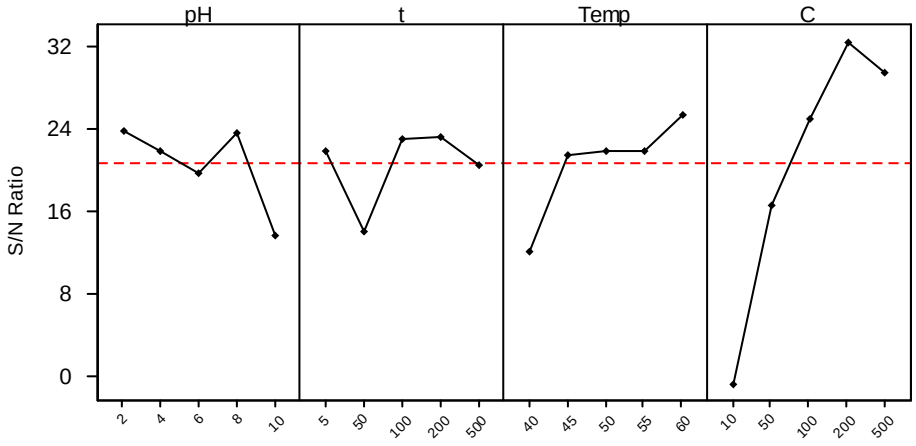

Fig. 3 The higher the better S/N graph for CR uptake onto BFA

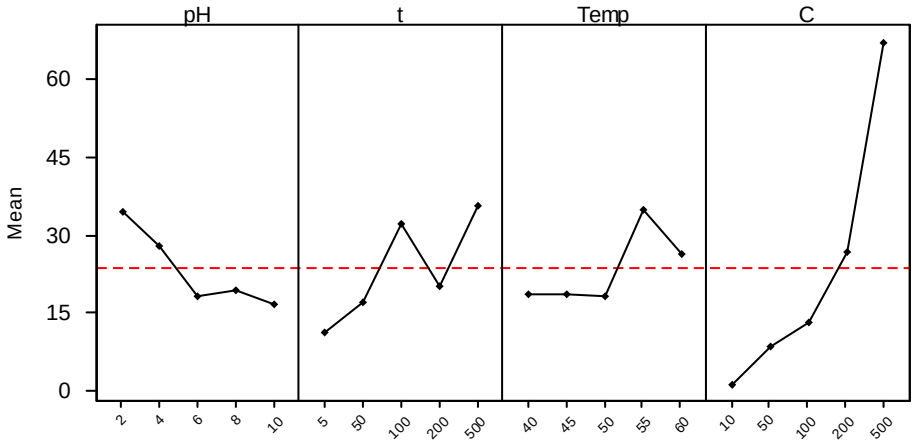

Fig. 4 The higher the better S/N graph for CR uptake onto RHA

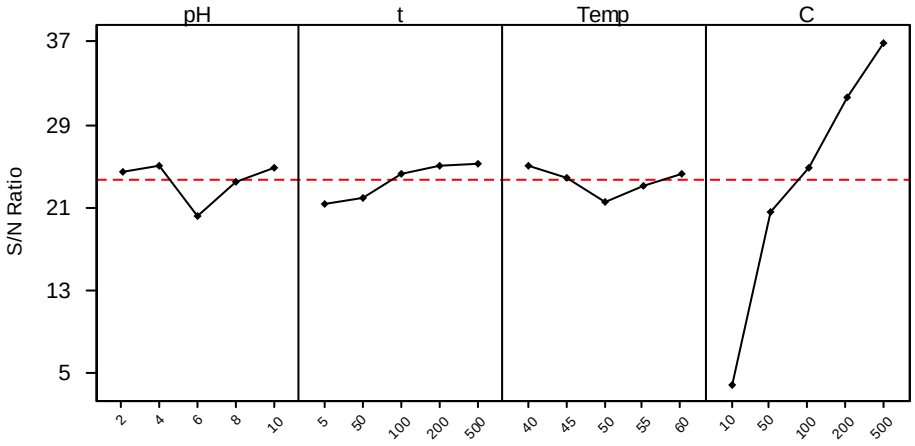

Fig. 5 The higher the better S/N graph for CR uptake onto CCA

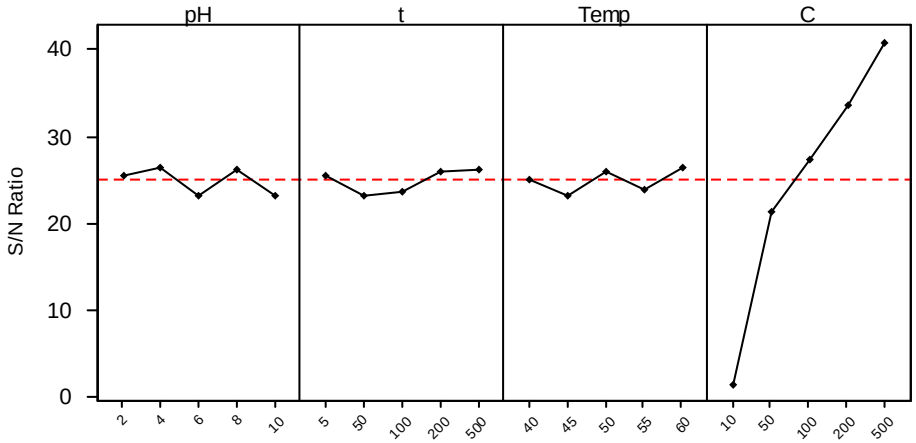

Fig. 6 The higher the better S/N graph for CR uptake onto FJE

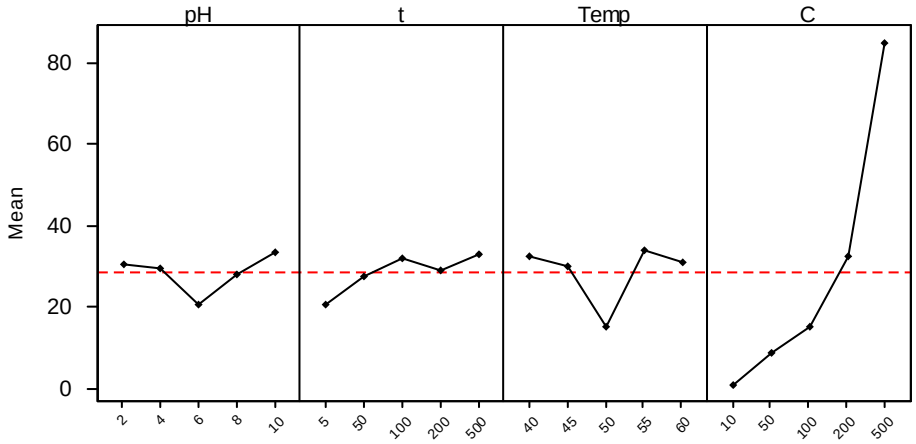

Fig. 7 The higher the better S/N graph for CR uptake onto BAEL

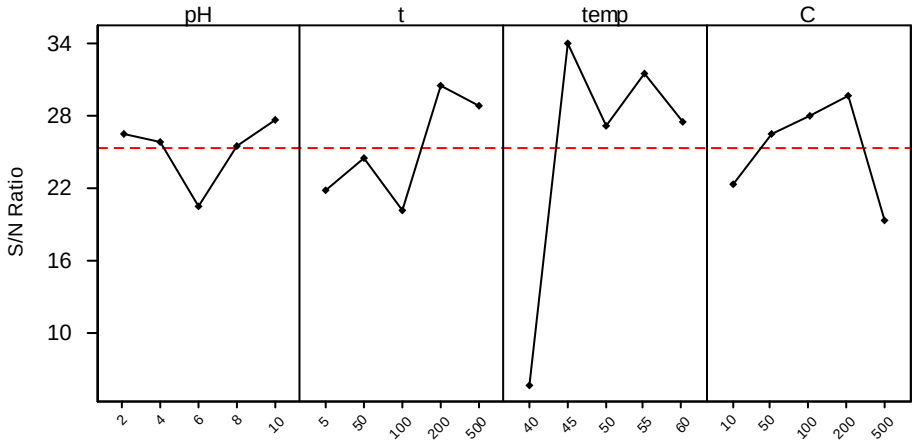

Fig. 8 The higher the better S/N graph for CR uptake onto ST

4.1 Analysis of the S/N ratio

In the Taguchi method, the term 'signal' represents the desirable value (mean) for the output characteristic and the term 'noise' represents the undesirable value (S.D.) for the output

characteristic. Therefore, the S/N ratio is the ratio of the mean to the S.D. Taguchi uses the S/N ratio to measure the quality characteristic deviating from the desired value. The S/N ratio η is defined as

$$\eta = -10 \log(\text{M.S.D}) \tag{2}$$

Where M.S.D. is the mean-square deviation for the output characteristic.

There are three categories of quality characteristics, i.e. the-lower-the-better, the higher- the-better, and the-nominal-the-better. To obtain optimal removal performance, the-higher-the-better quality characteristic was selected. The mean-square deviation (M.S.D.) for the-higher-the-better quality characteristic can be written as:

$$\text{M.S.D} = \frac{1}{\text{n}}\left(\sum_{i=1}^{n} \frac{1}{y_i^2}\right) \tag{3}$$

Where, n is the number of tests and y_i is the comparison variables in the i^{th} experiment.

Taguchi recommends analyzing the means and S/N ratio using conceptual approach that involves graphing the effects and visually identifying the factors that appear to be significant, without using ANOVA, thus making the analysis simple [M.S. Phadke,1989].

Table 5 shows the experimental results for CR removal onto various adsorbents used in the present study and their corresponding computed S/N ratio using eqs. (2) and (3). Since the experimental design is an orthogonal, it is then possible to separate out the effect of each parameter at different levels. For example, the mean S/N ratio for pH at levels 1, 2, 3, 4 and 5 can be calculated by averaging the S/N ratios for the experiments 1–6, 6–10, 11-15, 16-20 and 21-25, respectively. In similar manner, the mean S/N ratio for each level can be computed for other parameters. The mean S/N ratio for each level of parameters used in the present study is summarized in Table 6 and called the S/N response table. In addition, the total mean S/N ratio for the 25 experiments is also calculated and listed in same Table 6 for all the adsorbents. Figs. 1-8 show the S/N response graph for CR uptake onto different adsorbents. As shown in equ. (2) and (3), the greater is the S/N ratio, the smaller is the variance of CR uptake around the desired (the-higher-the-better) value. However, the relative importance amongst of the process

parameters for CR uptake still needs to be known so that optimal combinations of the process parameter levels can be determined more accurately. This will be discussed in the next section using the analysis of variance of the experimental data.

4.2 Analysis of variance

The purpose of the analysis of variance (ANOVA) is to investigate which design parameters significantly affect the quality characteristic. This is to accomplish by separating the total variability of the S/N ratios, which is measured by the sum of the squared deviations from the total mean S/N ratio, into contributions by each of the design parameters and the error. First, the total sum of squared deviations SST from the total mean S/N ratio η_m can be calculated as:

$$SS_T = \sum_{i=1}^{n} (\eta_i - \eta_m)^2 \qquad (4)$$

Where, n is the number of experiments in the orthogonal array and η_i is the mean S/N ratio for the i^{th} experiment.

The total sum of squared deviations SS_T is decomposed into two sources: the sum of squared deviations SS_d due to each design parameter and the sum of squared error SS_e. The percentage contribution by each of the design parameters in the total sum of squared deviations SS_T is a ratio of the sum of squared deviations SS_d due to each design parameter to the total sum of squared deviations SS_T [Yang and Tarng, 1998].

Statistically, there is a tool called an *F* test named after Fisher to see which design parameters have a significant effect on the quality characteristic. In performing the *F* test, the mean of squared deviations SS_m due to each design parameter needs to be calculated. The mean of squared deviations SS_m is equal to the sum of squared deviations SS_d divided by the number the *F*- test, the mean of squared deviations SS_m due to each design parameter needs to be calculated. The mean of squared deviations SS_m is equal to the sum of squared deviations SS_d divided by the number of degrees of freedom associated with the design parameter. Then, the F value for each design parameter is simply the ratio of the mean of squared deviations SS_m to the mean of

squared error. Usually, when F>4, it means that the change of the design parameter has a significant effect on the quality characteristic (Tarng and Yang, 1998).

Table 7 shows the results of ANOVA for CR-adsorbents system. It can be found that initial concentration of Congo red (CR) having the significant effect for CR uptake onto adsorbents used. Therefore, based on the S/N and ANOVA analysis, the optimal removal parameters for CR uptake are presented in table 8 for all the adsorption systems.

4.3 Confirmation tests

Once the optimal levels for the maximum uptake of CR onto adsorbents have been selected, the final step is to predict and verify the improvement of the quality characteristic using the optimal level of the design parameters. The estimated S/N ratio $\overline{\eta}$ using the optimal level of the design parameters for CR uptake can be calculated as (Tarng and Yang, 1998).

$$\overline{\eta} = \eta_m + \sum_{i=1}^{o} (\eta_i - \eta_m) \tag{5}$$

Where η_m is the total mean S/N ratio, η_i is the mean S/N ratio at the optimal level, and o is the number of the main design parameters that affect the CR removal characteristic. The estimated S/N ratio using the optimal removal parameters for CR uptake can then be obtained and the corresponding removal can also be calculated by using Eqs. (2) and (3). Table 8 shows the comparison of the predicted uptake with the actual uptake using the optimal removal parameters, good agreement between the predicted and actual CR uptake being observed. CR uptake values onto various adsorbents available in literature have been presented in (Table 3) for comparisons with the CR uptake value obtained in the present work.

4.4 Spent adsorbents

The exhausted low-cost adsorbents along with the sorbed CR can be separated from the solution (by filtration), dried and used as such or as fire briquettes to recover their energy value. The resulting bottom ash blended with cementations mixture can be used for making building blocks or it may be used to make fire bricks.

Table 5. Experimental results for CR uptake onto various adsorbents and their corresponding S/N ratio.

S.No	pH	t	T	C_o	$q_{e,PAC}$	SNR	$q_{e,GAC}$	SNR	$q_{e,BFA}$	SNR	$q_{e,RHA}$	SNR	$q_{e,CCA}$	SNR	$q_{e,FJE}$	SNR	$q_{e,BEL}$	SNR	$q_{e,ST}$	SNR
1	2	5	40	10	1.90	5.59	1.99	5.98	1.16	1.29	2.08	6.36	1.67	4.47	1.78	5.02	1.52	3.64	2.25	7.02
2	2	50	45	50	5.38	14.61	2.98	9.48	8.95	19.04	2.10	6.44	9.55	19.60	9.80	19.82	8.47	18.56	49.92	33.96
3	2	100	50	100	24.34	27.73	18.82	25.49	19.99	26.02	20.65	26.30	20.56	26.26	24.75	27.87	13.04	22.31	12.43	21.89
4	2	200	55	200	48.01	33.63	36.28	31.19	45.26	33.11	41.48	32.36	41.08	32.27	49.49	33.89	35.08	30.90	124.93	41.93
5	2	500	60	500	124.57	41.91	73.21	37.29	109.58	40.79	107.08	40.59	105.15	40.44	114.64	41.19	95.66	39.61	24.56	27.81
6	4	5	45	100	22.88	27.19	13.08	22.33	18.49	25.34	6.92	16.80	17.41	24.81	24.66	27.84	17.75	24.98	124.53	41.91
7	4	50	50	200	48.53	33.72	33.98	30.62	46.53	33.35	24.54	27.80	37.02	31.37	49.82	33.95	17.09	24.65	49.90	33.96
8	4	100	55	500	122.55	41.77	97.25	39.76	103.50	40.30	98.82	39.90	92.96	39.37	123.89	41.86	104.21	40.36	16.68	24.44
9	4	200	60	10	2.04	6.20	2.50	7.96	2.07	6.32	1.80	5.11	2.48	7.87	2.46	7.83	2.31	7.27	12.43	21.89
10	4	500	40	50	11.68	21.35	6.68	16.50	1.70	4.61	9.01	19.09	12.26	21.77	12.21	21.74	8.92	19.01	2.30	7.24
11	6	5	50	500	124.42	41.90	3.88	11.78	34.81	30.83	36.42	31.23	17.31	24.76	101.81	40.16	36.87	31.33	1.77	4.95
12	6	50	55	10	2.05	6.22	0.81	-1.83	0.39	-8.18	0.63	-4.01	0.71	-3.02	0.55	-5.12	0.62	-4.15	24.81	27.89
13	6	100	60	50	11.84	21.47	10.34	20.29	12.24	21.76	11.31	21.07	10.62	20.52	12.37	21.85	9.69	19.73	24.76	27.87
14	6	200	40	100	24.70	27.85	15.60	23.86	14.54	23.25	4.49	13.04	21.37	26.60	18.89	25.52	16.53	24.37	2.48	7.88
15	6	500	45	200	47.11	33.46	28.59	29.12	38.77	31.77	38.83	31.78	41.05	32.27	49.61	33.91	40.05	32.05	49.62	33.91
16	8	5	55	50	11.96	21.55	11.52	21.23	10.77	20.64	11.57	21.27	11.71	21.37	12.21	21.73	11.22	21.00	12.40	21.87

17	8	50	60	100	23.37	27.37	24.56	27.80	22.21	26.93	10.95	20.79	11.08	20.89	24.56	27.80	9.60	19.65	22.03	26.86
18	8	100	40	200	46.10	33.27	19.19	25.66	41.06	32.27	29.11	29.28	35.09	30.90	49.37	33.87	34.04	30.64	2.02	6.09
19	8	200	45	500	92.16	39.29	72.52	37.21	70.55	36.97	44.40	32.95	85.17	38.61	116.30	41.31	85.41	38.63	95.20	39.57
20	8	500	50	10	1.64	4.27	2.03	6.15	1.32	2.41	1.62	4.19	2.00	6.02	2.10	6.42	1.95	5.80	49.79	33.94
21	10	5	60	200	34.52	30.76	15.46	23.78	40.68	32.19	0.99	-0.09	40.12	32.07	48.17	33.66	38.23	31.65	46.88	33.42
22	10	50	40	500	118.19	41.45	104.15	40.35	0.97	-0.26	48.72	33.75	120.06	41.59	97.72	39.80	103.13	40.27	1.05	0.39
23	10	100	45	10	2.15	6.66	1.91	5.62	0.59	-4.58	1.60	4.08	1.66	4.39	0.48	-6.38	0.20	-13.98	11.18	20.97
24	10	200	50	50	11.69	21.36	10.17	20.15	7.52	17.52	9.29	19.36	10.15	20.13	12.35	21.84	7.54	17.55	124.91	41.93
25	10	500	55	100	23.26	27.33	23.08	27.26	16.19	24.18	23.12	27.28	20.53	26.25	24.58	27.81	20.51	26.24	124.54	41.91

Table 6. Response table for average S/N ratio for CR uptake

Symbol	variables	PAC							GAC						
		Mean S/N ratio							Mean S/N ratio						
		1	2	3	4	5	Maximum-Minimum	Process influencing Rank	1	2	3	4	5	Maximum-Minimum	Process influencing Rank
pH	Hydrogen ions strength	24.69	26.04	26.18	25.15	25.51	1.49	4	21.88	23.44	16.65	23.61	23.44	6.79	3
t	Time (min)	25.39	24.67	26.17	25.66	25.66	1.50	3	17.02	21.29	23.37	24.08	23.27	7.78	2
T	Temperature (^oC)	25.90	24.24	25.79	26.10	25.54	1.85	2	22.47	20.76	18.84	23.53	23.43	4.69	4
C_o	CR concentration (mg/l)	5.78	20.06	27.49	32.96	41.26	35.47	1	4.78	17.53	25.36	28.28	33.28	28.5	1
		BFA							RHA						
pH	Hydrogen ions strength	24.05	21.98	19.88	23.84	13.80	10.24	3	34.67	28.21	18.33	19.53	16.74	17.93	3
t	Time (min)	22.05	14.17	23.1512	23.43	20.75	9.26	4	11.59	17.38	32.29	20.29	35.93	24.33	2
T	Temperature (^oC)	12.23	21.70	22.02	22.01	25.59	13.36	2	18.68	18.77	18.50	35.12	26.42	16.62	4
C_o	CR concentration (mg/l)	-0.54	16.71	25.14	32.53	29.72	33.08	1	1.54	8.65	13.22	26.99	67.08	65.54	1
		CCA							FJE						
pH	Hydrogen ions strength	24.60	25.03	20.22	23.55	24.88	4.81	2	25.55	26.64	23.26	26.22	23.34	3.37	2
t	Time (min)	21.49	22.08	24.28	25.09	25.34	3.85	3	25.68	23.25	23.81	26.07	26.21	2.96	4

T	Temperature (^{o}C)	25.06	23.93	21.70	23.24	24.35	3.35	4	25.19	23.30	26.04	24.03	26.46	3.16	3
C_o	CR concentration (mg/l)	3.94	20.67	24.96	31.77	36.95	33.00	1	1.55	21.39	27.37	33.85	40.86	39.30	1
		BAEL							ST						
pH	Hydrogen ions strength	30.75	30.05	20.75	28.44	33.92	13.17	3	26.52	25.88	20.50	25.66	27.72	7.22	4
t	Time (min)	21.11	27.78	32.23	29.37	33.41	12.30	4	21.83	24.61	20.25	30.64	28.96	10.38	3
T	Temperature (^{o}C)	32.82	30.37	15.29	34.32	31.09	19.03	2	5.72	34.06	27.33	31.60	27.56	28.34	1
C_o	CR concentration (mg/l)	1.32	9.16	15.48	32.89	85.05	83.73	1	22.34	26.57	28.08	29.86	19.43	10.43	2

Table 7. Analysis of Variance (ANOVA) for q_e, using Adjusted SS for Tests

	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
PAC	pH	1	75	75	75	1.76	0.199
	t	1	9	9	9	0.21	0.655
	temp	1	13	13	13	0.31	0.583
	C	1	42177	42177	42177	993.25	0.000
	Error	20	849	849	42		
	Total	24	43123				
	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
GAC	pH	4	1222.1	1222.1	305.5	0.91	0.503
	t	4	1738.5	1738.5	434.6	1.29	0.350
	temp	4	1124.3	1124.3	281.1	0.84	0.539
	C	4	14475.8	14475.8	3619.0	10.77	0.003
	Error	8	2688.0	2688.0	336.0		
	Total	24	21248.7				
	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
BFA	pH	4	1987.8	1987.8	497	1.26	0.361
	t	4	1370.4	1370.4	342.6	0.87	0.522
	temp	4	2139.8	2139.8	534.9	1.36	0.330
	C	4	13488.2	13488.2	3372	8.55	0.005
	Error	8	3155.3	3155.3	394.4		
	Total	24	22141.5				
	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
RHA	pH	4	1176.4	1176.4	294.1	1.66	0.251
	t	4	2106.6	2106.6	526.6	2.98	0.089
	temp	4	1071.1	1071.1	267.8	1.51	0.286
	C	4	13599.9	13599.9	3400.0	19.21	0.000
	Error	8	1416.0	1416.0	177.0		
	Total	24	19369.9				

	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
CCA	pH	4	1233.8	1233.8	308.5	0.89	0.510
	t	4	1147.7	1147.7	286.9	0.83	0.541
	temp	4	1243.8	1243.8	311.0	0.90	0.506
	C	4	21562.9	21562.9	5390.7	15.63	0.001
	Error	8	2759.7	2759.7	345.0		
	Total	24	27947.9				

	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
FJE	pH	4	140.7	140.7	35.2	1.89	0.206
	t	4	103.5	103.5	25.9	1.39	0.320
	temp	4	111.6	111.6	27.9	1.50	0.290
	C	4	38300.1	38300.1	9575	514.53	0.000
	Error	8	148.9	148.9	18.6		
	Total	24	38804.7	38804.7			

	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
BAEL	pH	4	482.6	482.6	120.7	0.68	0.623
	t	4	467.5	467.5	116.9	0.66	0.635
	temp	4	1184.3	1184.3	296.1	1.68	0.247
	C	4	22496.8	22496.8	5624.2	31.86	0.000
	Error	8	1412.0	1412.0	176.5		
	Total	24	26043.3				

	Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
ST	pH	4	4330	4330	1083	0.71	0.606
	t	4	9737	9737	2434	1.60	0.264
	temp	4	14009	14009	3502	2.30	0.146
	C	4	5309	5309	1327	0.87	0.520
	Error	8	12159	12159	1520		
	Total	24	45545				

Table 8. Process parameters for CR batch adsorption study using Taguchi method.

System	Parameters				q_e (mg/g) Actual value	*SNR*	Optimized value (mg/g)
	pH	t	T	C_o			
CR-PAC	2	50	60	500	124.57	41.91	124.57±2.53
CR-GAC	10	50	40	500	104.50	40.35	104.5±1.73
CR-BFA	2	500	60	500	109.58	40.79	109.58±0.13
CR-RHA	2	500	60	500	107.08	40.59	107.08±0.41
CR-CCA	10	50	40	500	120.06	41.59	120.06±0.86
CR-FJE	4	100	55	500	123.89	41.86	123.89±0.24
CR-BAEL	4	100	55	500	104.21	40.36	104.21±0.96
CR-ST	*2*	*500*	*60*	*500*	*124.93*	*41.93*	124.93±2.57
-do-	*4*	*5*	*45*	*100*	*124.53*	*41.91*	124.53±1.93
-do-	*10*	*200*	*50*	*50*	*124.91*	*41.93*	124.91±0.56
-do-	*10*	*50*	*55*	*100*	*124.54*	*41.91*	124.54±2.45

Table 9. Surface area and PZC of respective adsorbents

Material	Surface area of adsorbent (m^2/g)	Point of zero charge
GAC	462.67	7.8
BAEL	391.35	9.7
RHA	24.28	9.5
BFA	17.38	11
FJE	109	9
PAC	1196.85	9.7
CCA	431.72	8
ST	-	6

Chapter-5

CHARACTERIZATION OF ADSORBENTS

5. CHARACTERIZATION OF ADSORBENTS

5.1 Surface Area

The BET surface area of the PAC, GAC, BFA, RHA, CCA, FJE, BAEL and ST were determined and tabulated in Table 9. The surface areas of the adsorbents used in the present work are comparable with the adsorbents available in literature (Table 4).

5.2 Point of zero charge (PZC)

The PZC is an important property of carbon–water interfaces. The PZC is defined as the pH at which the carbon surface has no charge in the absence of specific adsorption. The carbon surface is positively charged at pH values below the pH_{PZC} and negatively charged at pH values above the pH_{PZC} (León and Radovic, 1994; Radovic et al. 2001). The point of zero charge was estimated using solid addition method for all the commercial and low cost laboratory prepared adsorbents (detail procedure given in chapter 2), and their obtained values has been Tabulated in Table 9. *Appendix A* shows the PZC graphs for adsorbents used in the present study.

5.3 FTIR and SEM

The FTIR spectra and SEM of virgin and CR loaded commercial and laboratory prepared low cost are given in *Appendix B & C*.

FTIR Analysis

To determine which functional groups were responsible for CR uptake, an adsorption FTIR analysis of these eight adsorbents was performed using KBr disk. The spectra displayed a number of peaks, indicating the complex nature of the material examined. FTIR analysis shows that adsorption peak around 3429 cm^{-1} which is indicative of existence of hydroxyl groups and peak observed at 2760 cm^{-1} can be assigned to the C-H group. The peak observed at 1703 cm^{-1} is due to CO and the peak at the1612 cm^{-1} is due to C=C stretching that can be attributed to the aromatic C-C bond.

SEM Analysis

The surface morphology of these eight adsorbents was observed under SEM analysis. The SEM micrographs presented in appendix show the surface texture and porosity of the virgin and loaded adsorbent particles. It was found that the surface texture of the virgin adsorbents changes drastically after CR loading in case of all the eight adsorbents.

Chapter-6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSION

The following conclusion can be drawn from the present study

- The high uptake of CR onto laboratory prepared adsorbents proves the efficacy of low cost adsorbents, when it is compare with commercial grade adsorbents used in the present work as well as available in literature.
- Higher the F value or lesser the p value more the predominating factor in the CR uptake process. The Ranking of process variables can be done based on their respective p-values.
- Among all the tested adsorbents, ST was found to be the best one because of its high uptake capacity and its good flexibility for selecting the process variables for CR removal.
- Confirmatory test on optimum conditions indicates that the CR uptake differ with small value.

RECOMMENDATIONS

The following recommendation can be made from the present studies

- Kinetic studies must be performed to visualize the rate of CR removal onto used adsorbents.
- Equilibriums studies must be performed to obtain the maximum sorption of CR onto used adsorbents.
- Detail information about characterization of commercial and laboratory prepared adsorbents for FTIR, SEM, and TGA etc must be performed.
- CR desorption studies must also be performed.

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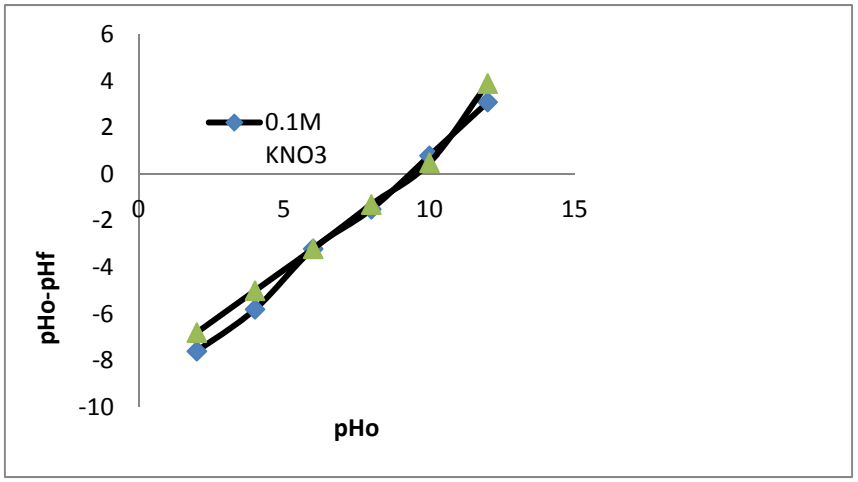
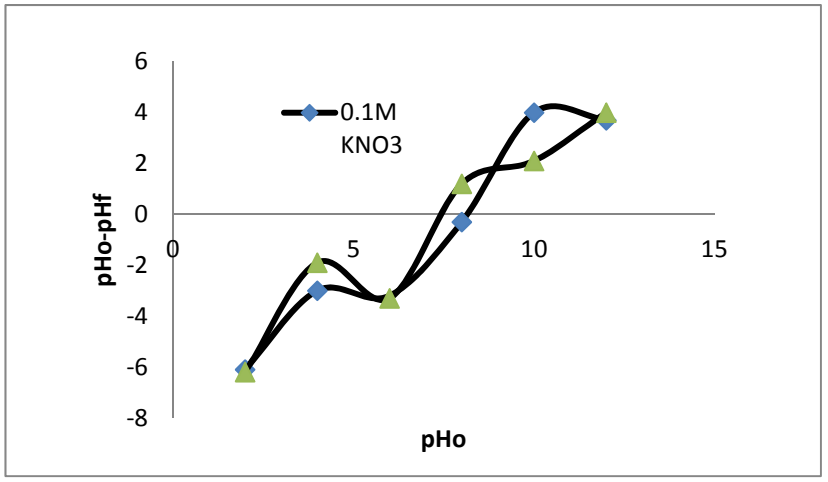
Appendix A

Point of zero charge graphs



Point of zero charge graph for PAC



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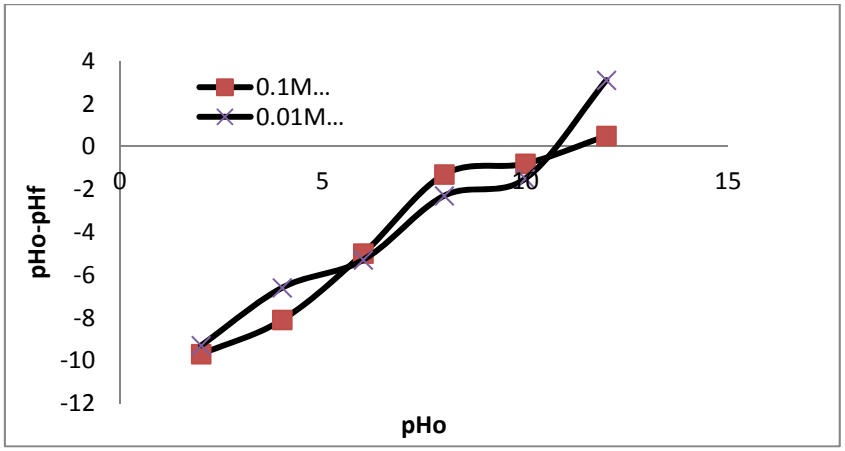
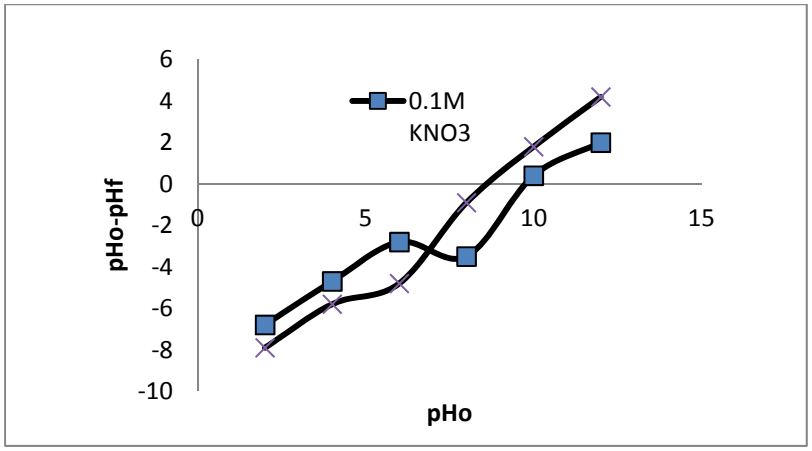
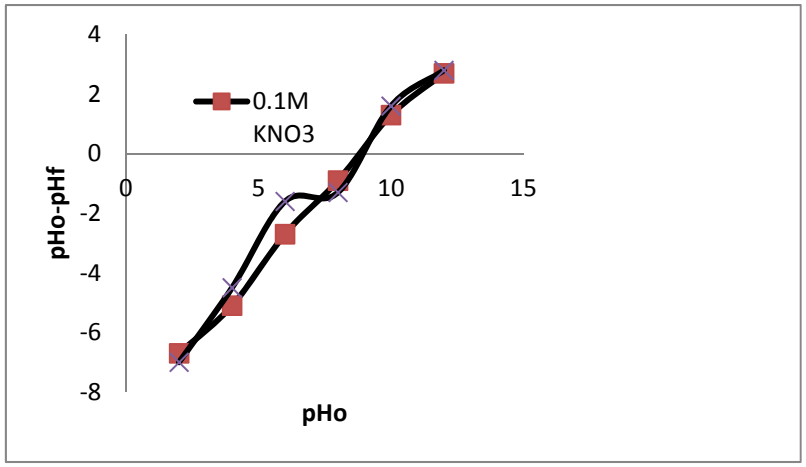


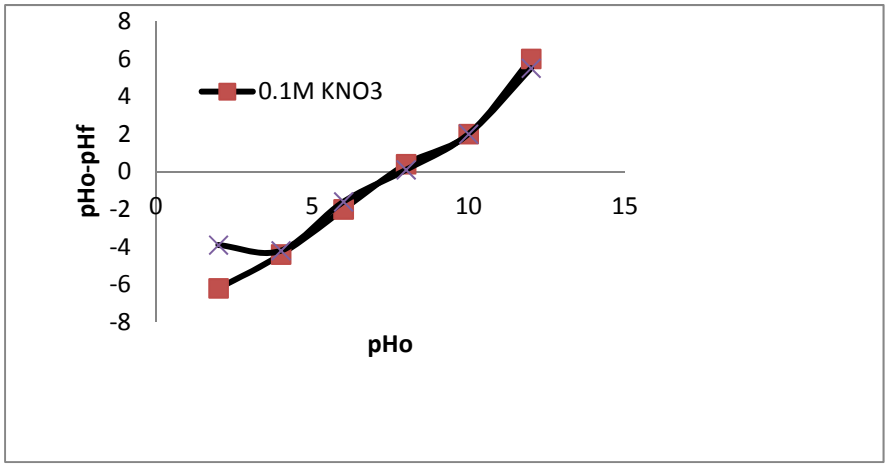
Point of zero charge graph for BFA



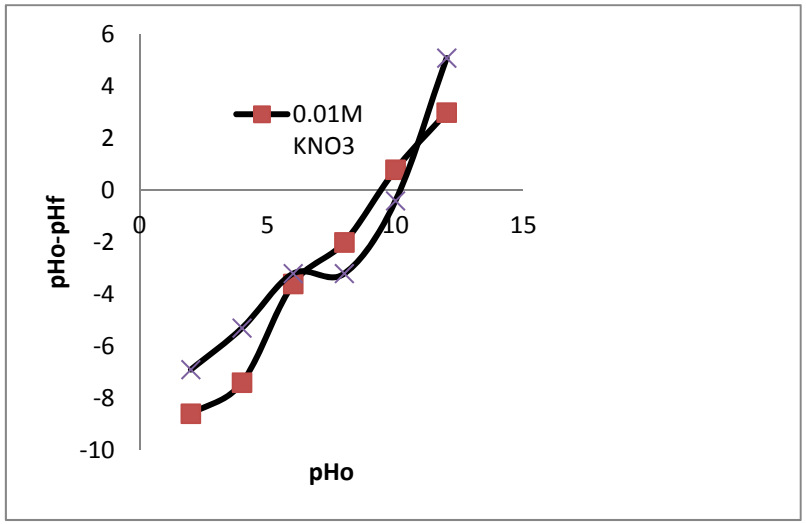
Point of zero charge graph for RHA



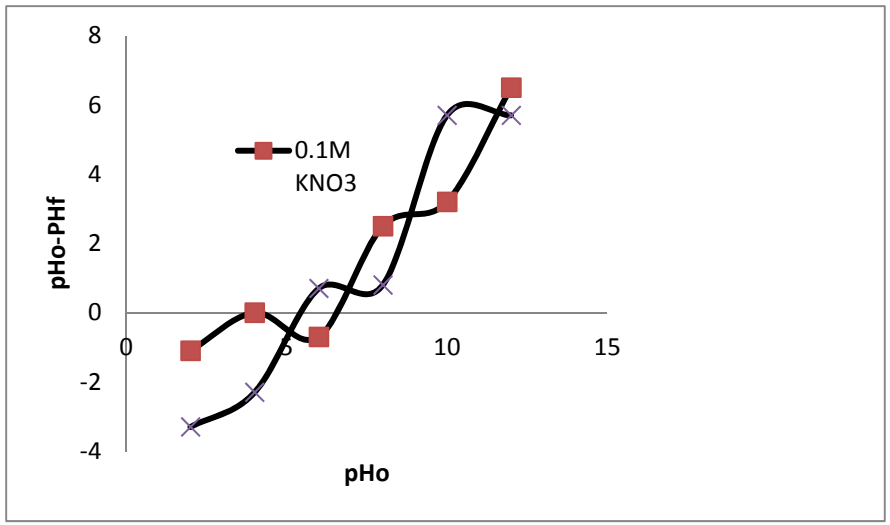
Point of zero charge graph for FJE



Point of zero charge graph for CCA



Point of zero charge graph for BAEL

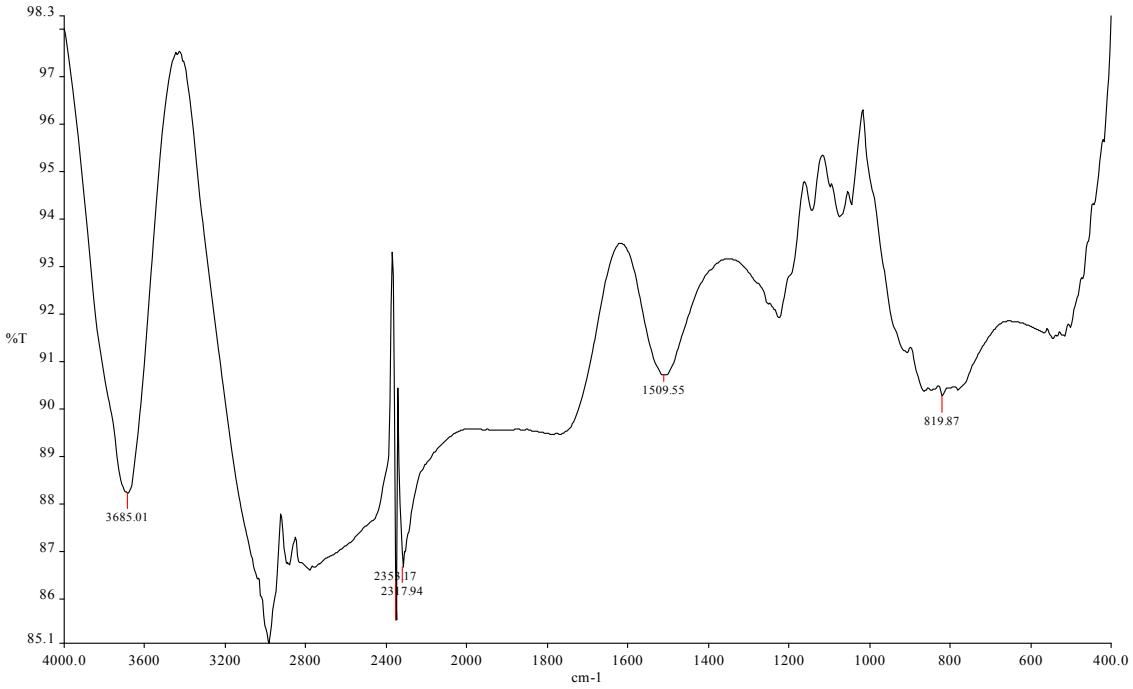


Point of zero charge graph for ST

Appendix B

FTIR Spectra of virgin & CR-loaded adsorbents

FTIR spectra of virgin adsorbents



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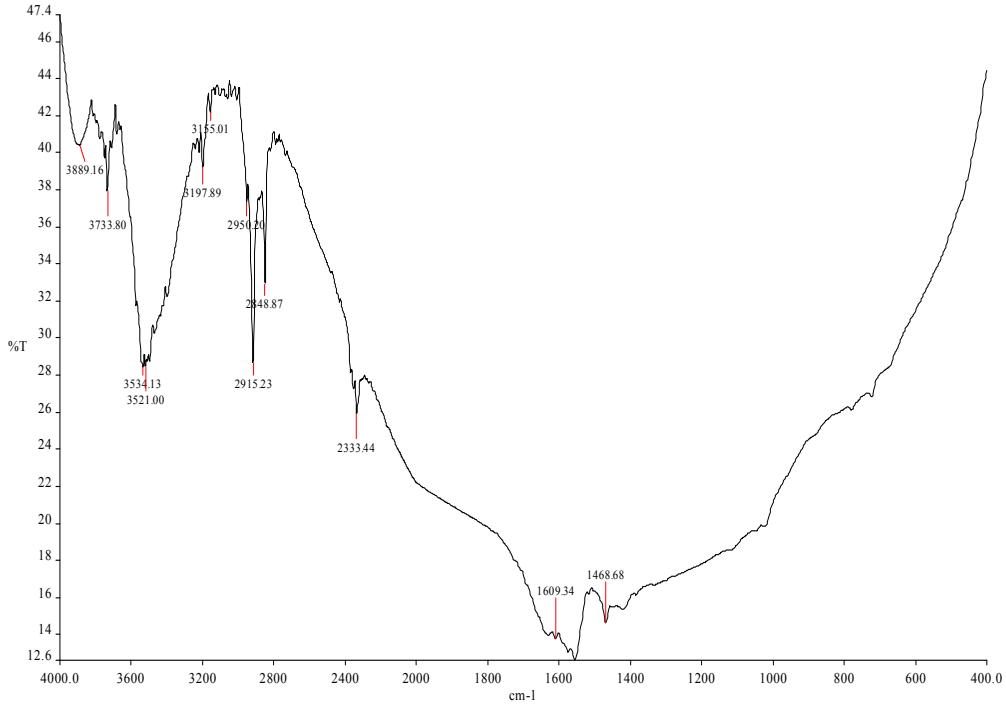

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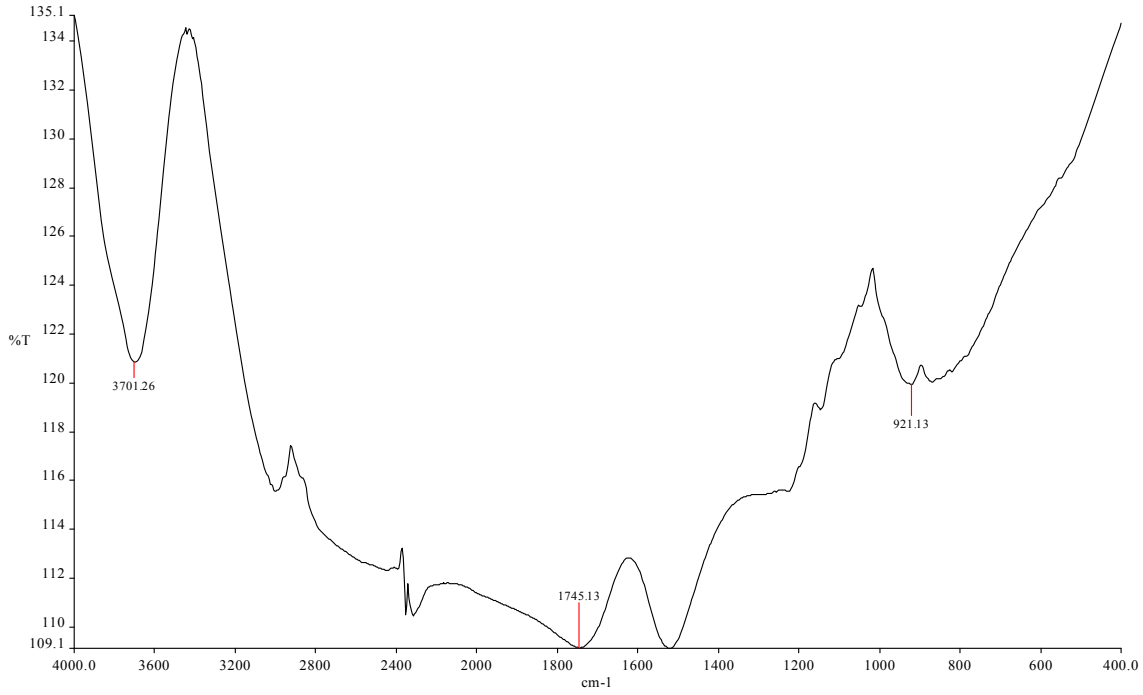
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132
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128
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124
122
120
118
116
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110
109.1
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1745.13
921.13
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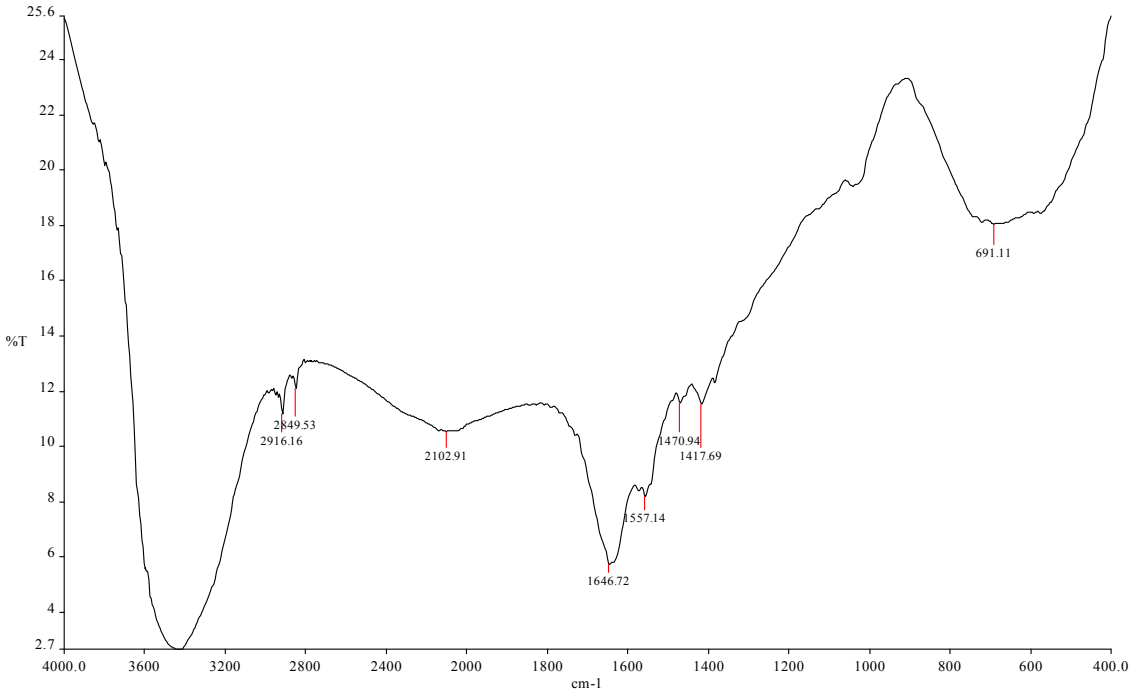
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1

RHA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22
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8
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1417.69
691.11
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2000
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1600
1400
1200
1000
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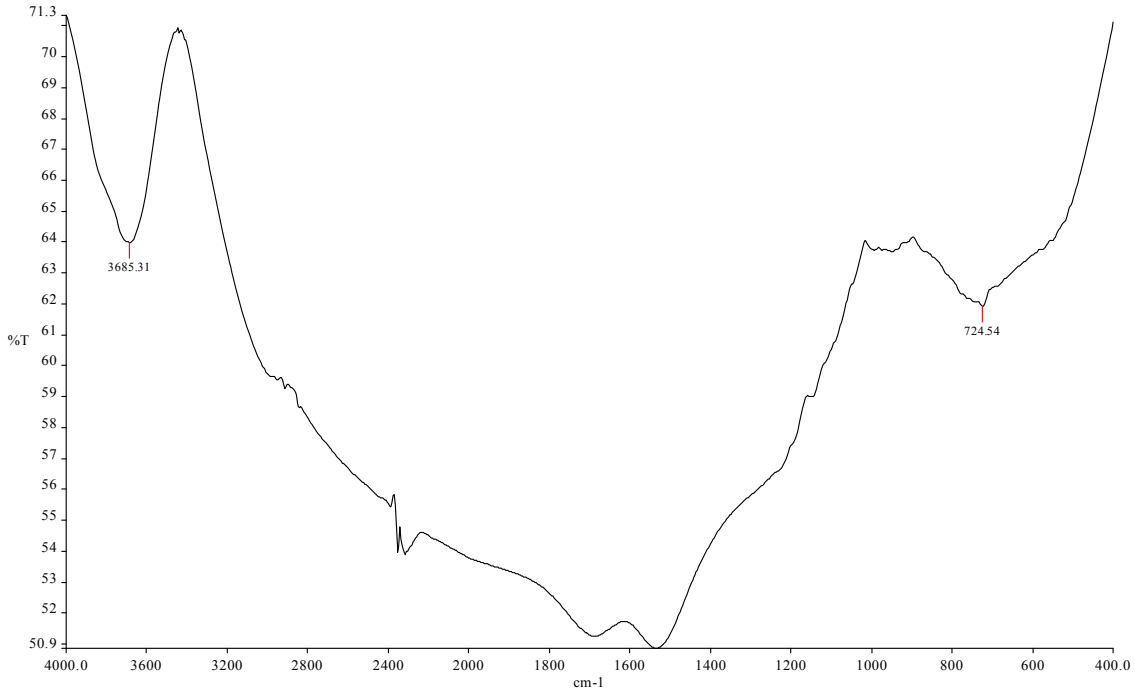
400.0
cm-1

BFA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50.9
%T
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724.54
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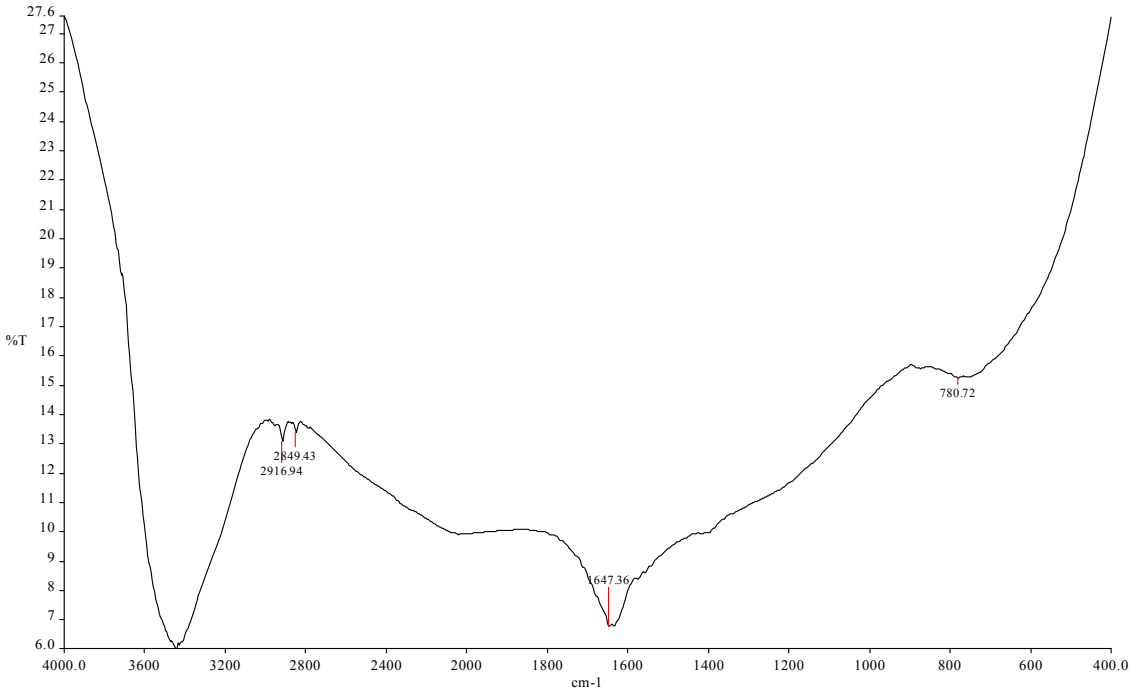
1000
800
600
400.0
cm-1

FJE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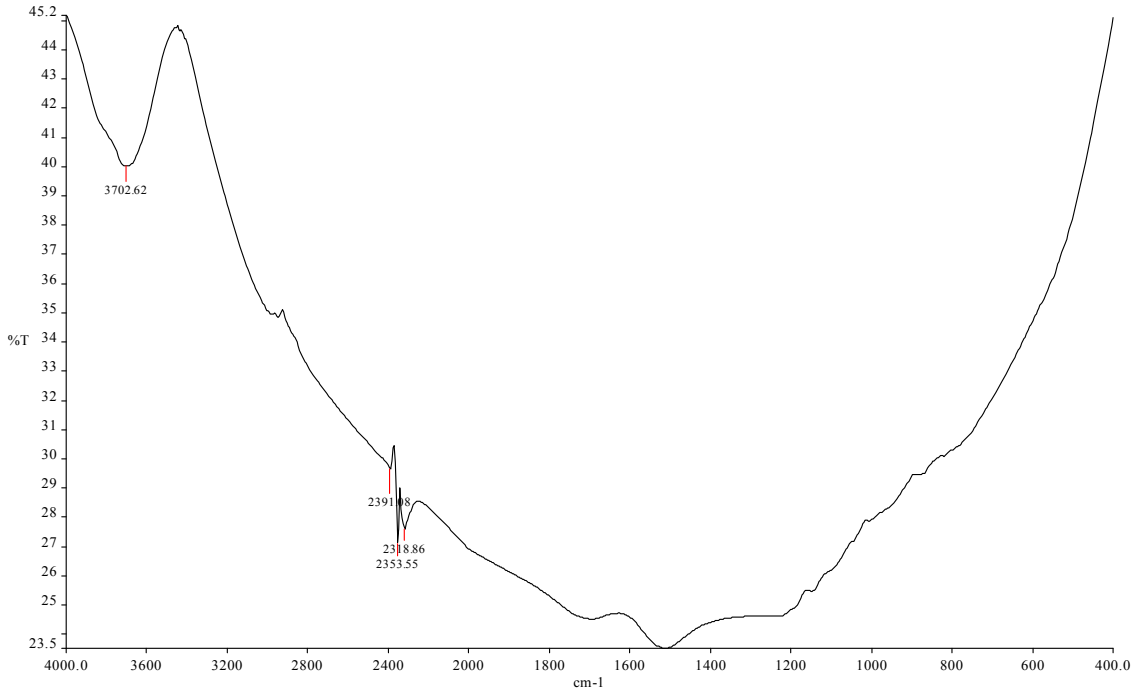
400.0
cm-1

PAC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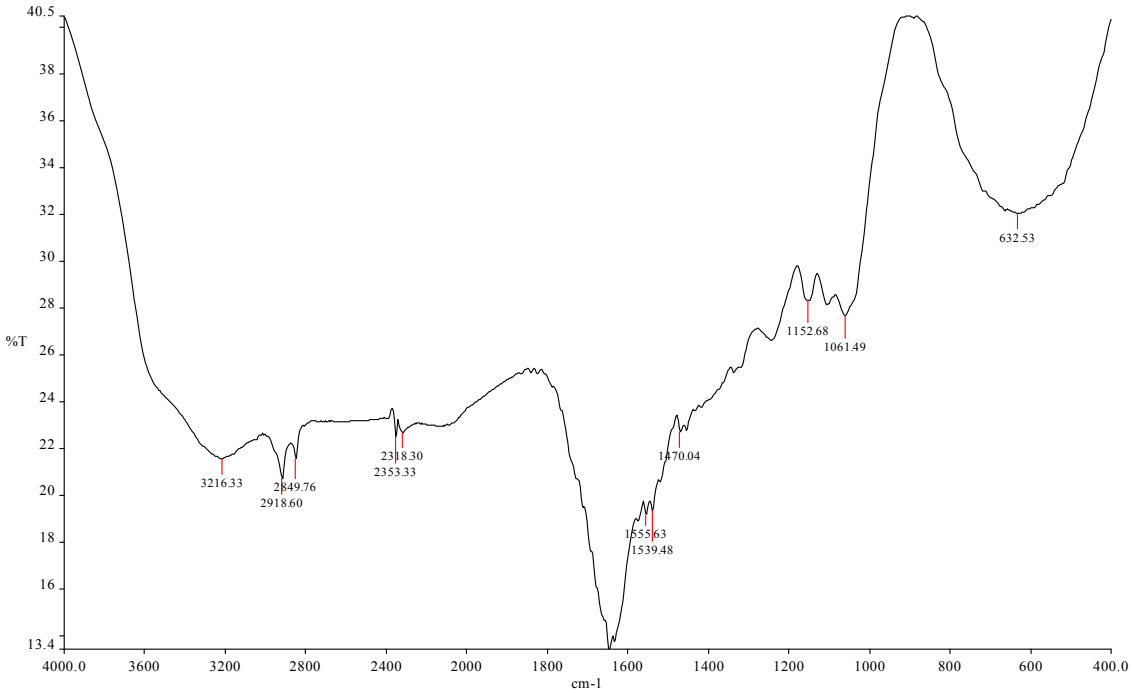
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1539.48
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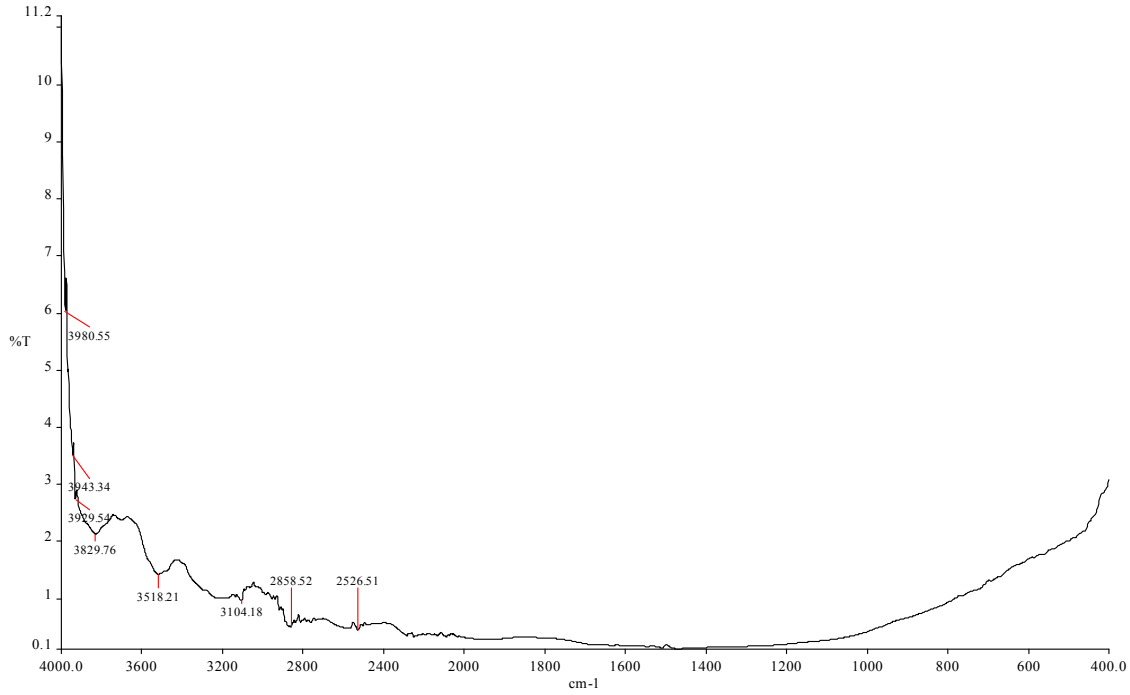
1061.49
632.53

ST

FTIR spectra of CR loaded adsorbents



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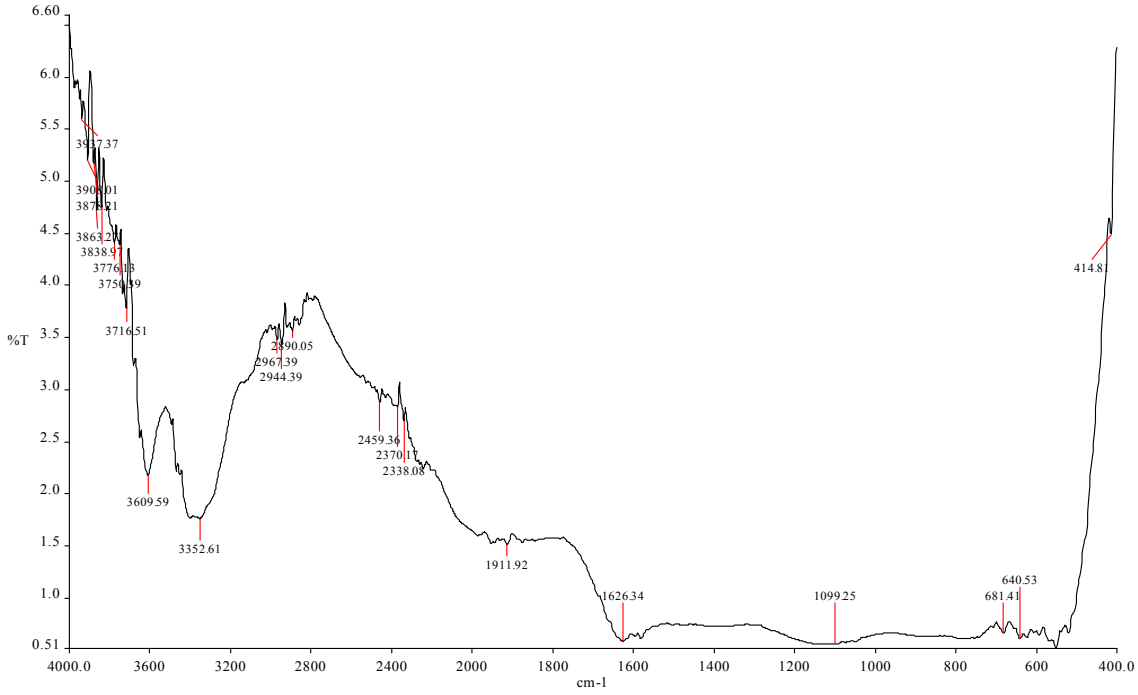

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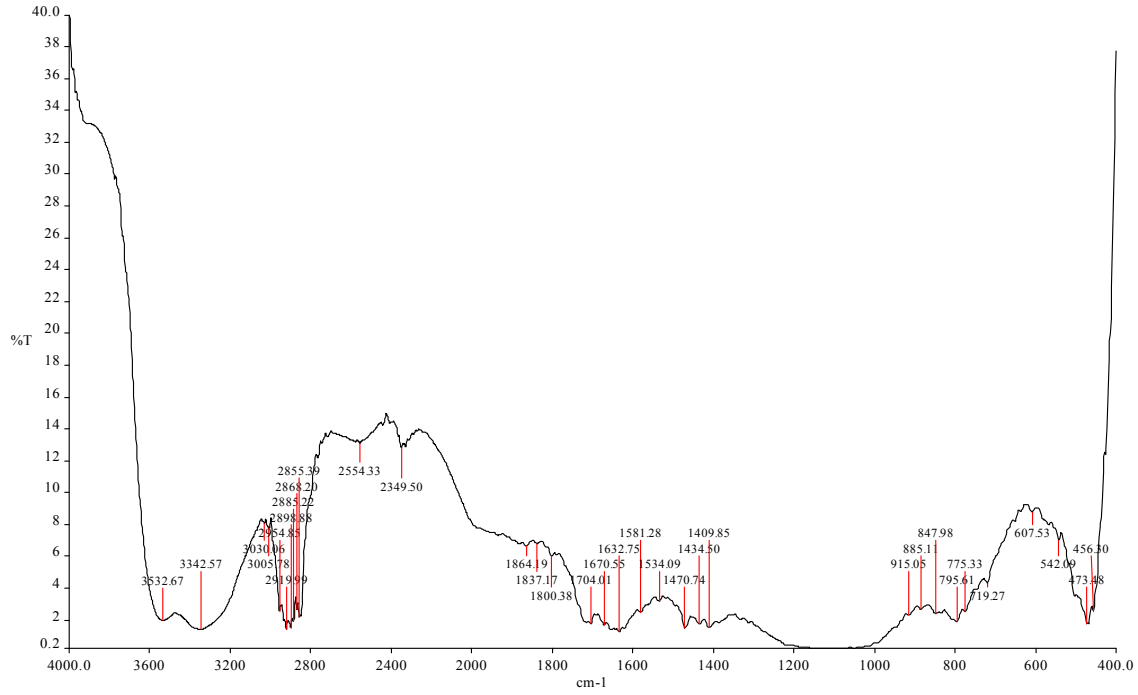
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cm-1
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3030.06
3005.78
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2898.88
2954.85
2554.33
2349.50
1864.19
1837.17
1800.38
1704.01
1670.55
1632.75
1581.28
1534.09
1470.74
1434.50
1409.85
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885.1
847.98
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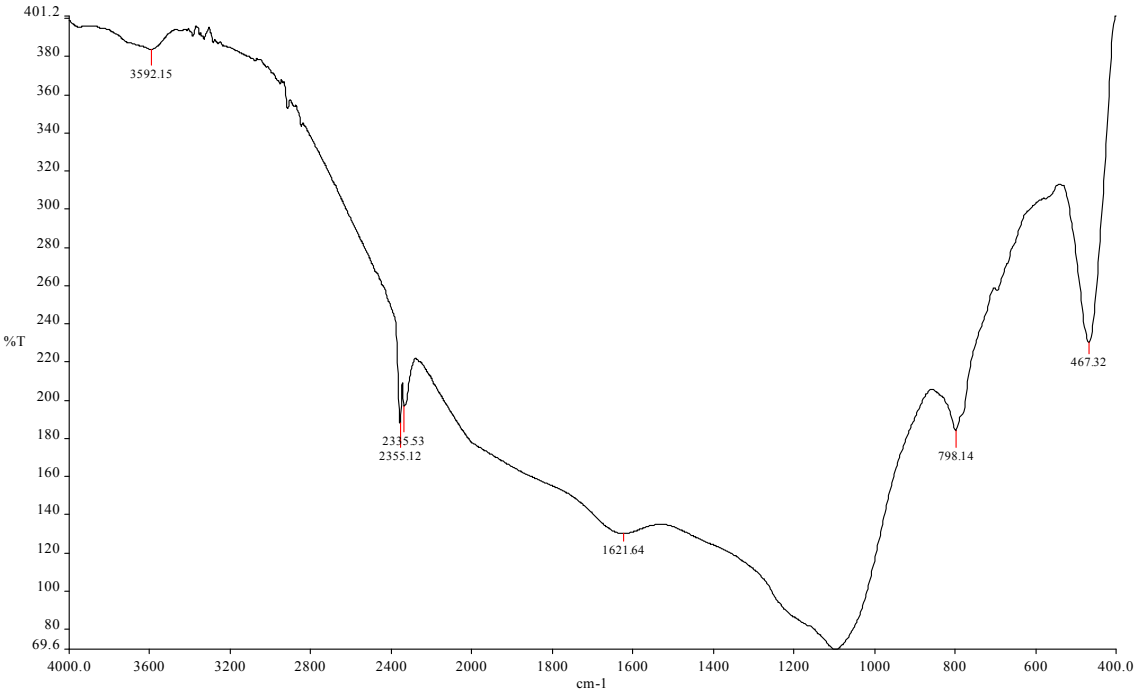
775.33
719.27
607.53
542.09
473.08
456.30

RHA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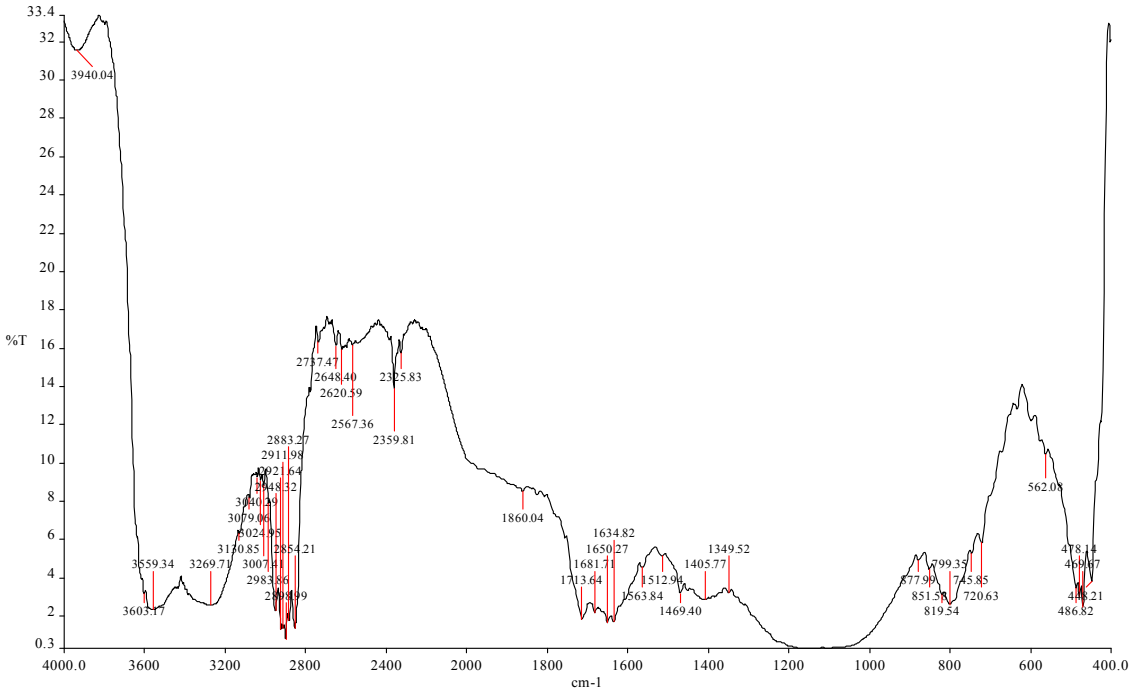
798.14
467.32

BFA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2737.47
2648.40
2620.59
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2359.81
1860.04
1634.82
1650.27
1681.71
1713.64
1563.84
1512.94
1469.40
1405.77
1349.52
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819.54
799.35
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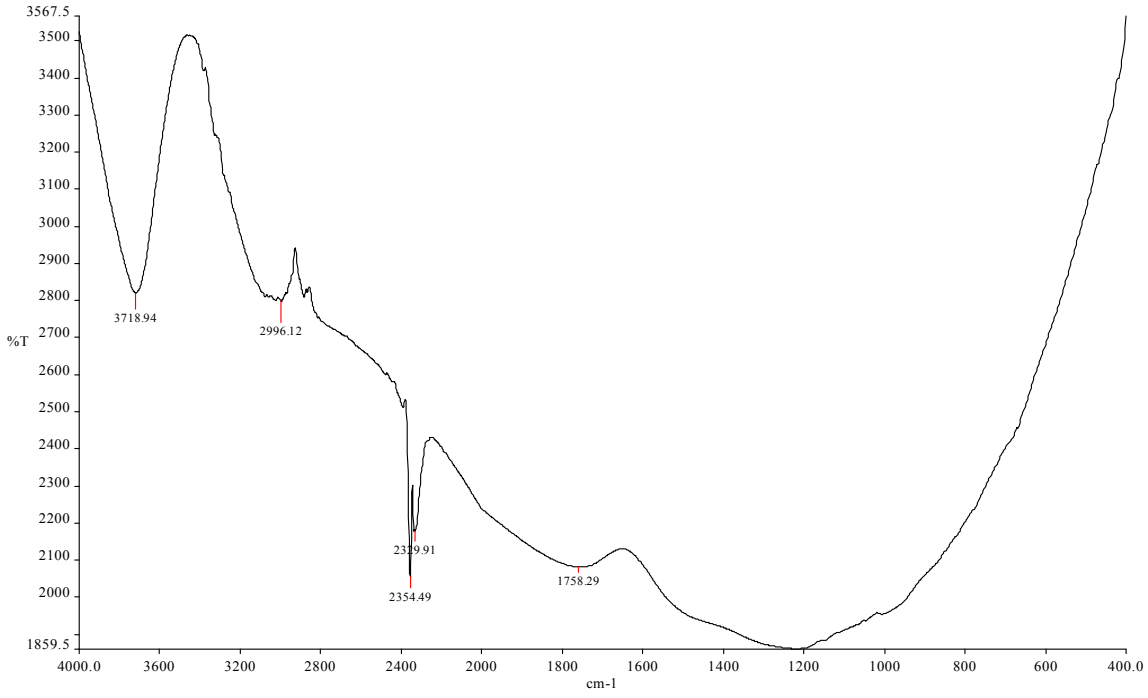
720.63
562.08
478.14
469.47
448.21
486.82

FJE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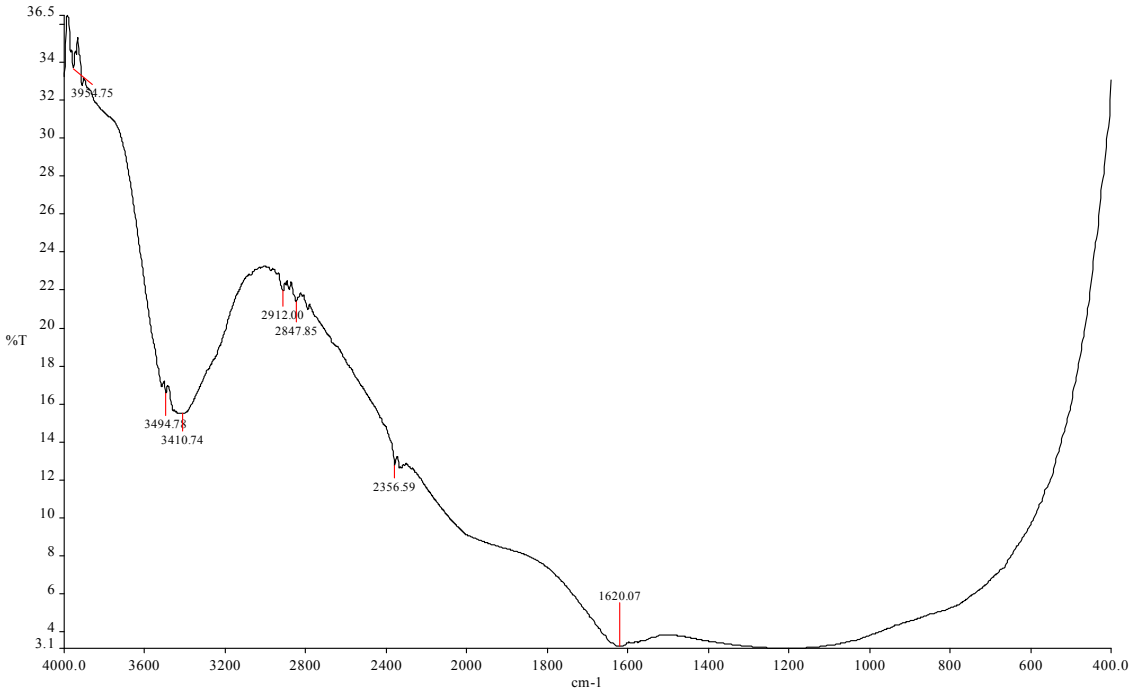
2996.12
2329.91
2354.49
1758.29

PAC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2912.00
2847.85
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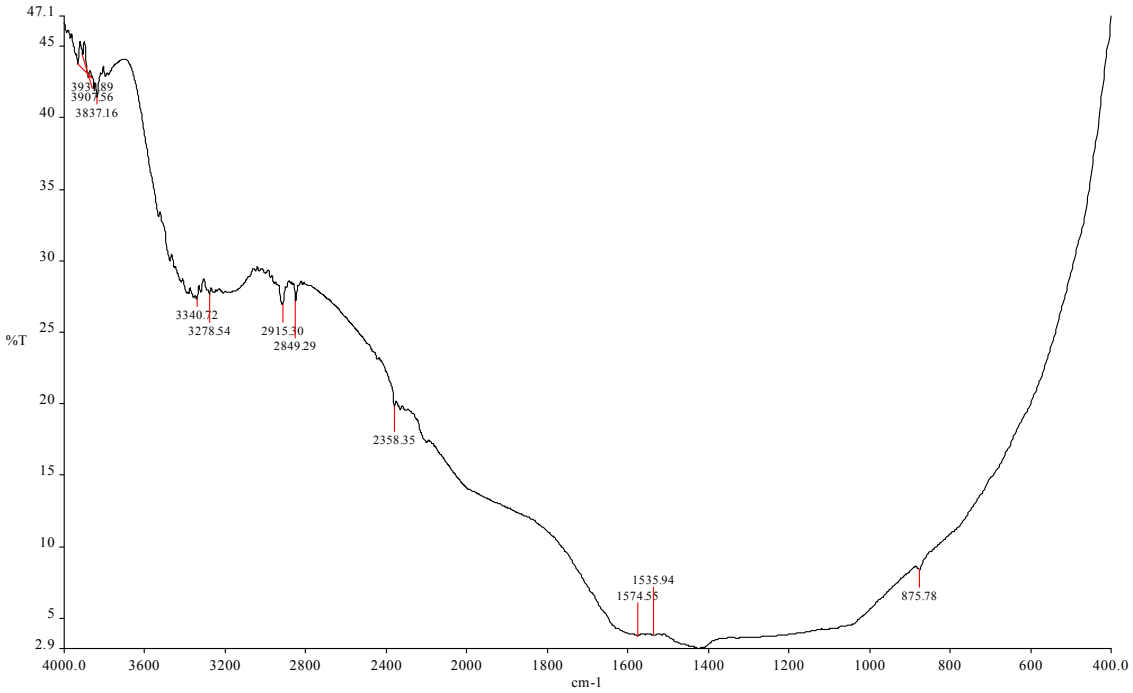
1620.07

CCA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cm-1
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3278.54
2915.30
2849.29
2358.35
1535.94
1574.55
875.78

ST

Functional groups representing correspond to wave number

Wave number. in cm^{-1}	Virgin PAC	CR Loaded PAC	Virgin GAC	CR Loaded GAC	Virgin BFA	CR Loaded BFA	Virgin RHA	CR Loaded RHA
3300-3600	_	_	_	O-----H (alcohol)	_	O--H (alcohol)	_	O-----H (alcohol)
2500-3000	O-----H (carboxylic acid)	O-----H (carboxylic acid)	_	O------H (carboxylic acid)	O-----H (carboxylic acid)	_	_	O--H (carboxylic acid)
3200-3500	_	_	_	_	_	_	_	N-----H
3300	_	_	_	_	_	_	_	_
3000-3100	_	_	_	_	_	_	_	==C-----H
2800-3000	_	_	_	_	_	_	_	C—H(sp3 carbon)
2250-2220	_	_	_	_	_	_	_	_
2100-2260	_	_	_	_	C≡≡C(alkyne)	_	_	_
1680-1820		C==O	_	_	_	_	C==O	C==O
1600-1650	C===C	_	_	_	C===C	C===C	_	C===C
~1600	_	_	_	_	_	_	_	_
1200	_	_	_	_	_	_	_	_
1050-1150	_	_	_	_	_	_	_	_
690 and750	_	_	_	_	Phenyl group	_	_	_

Cont.

Wave number cm^{-1}	Virgin CCA	CR Loaded CCA	Virgin FJE	CR Loaded FJE	Virgin BAEL	CR Loaded BAEL	Virgin ST	CR Loaded ST
3300-3600	_	O-----H (alcohol)	_	O-----H (alcohol)	_	O--H (alcohol)	_	O--H (alcohol)
2500-3000	_	O-----H (carboxylic acid)	_	O--H (carboxylic acid)	_	O--H (carboxylic acid)	O--H (carboxylic acid)	O--H (carboxylic acid)
3200-3500	_	N-----H	_	N-----H	_	N-----H	N-----H	N-----H
3300	_	_	_		_	_	_	_
3000-3100	_	_	_	==C-----H	_	_	_	_
2800-3000	_	C—H(sp3 carbon)	_	C—H(sp3 carbon)	_	C—H(sp3 carbon)	_	_
2250-2220	_	_	_	_	_	_	_	_
2100-2260	_	_	_	_	_	_	_	_
1680-1820	_	_	_	C==O	_		_	_
1600-1650	_	C===C	_	C===C	_	C===C	_	_
~1600	_	_	_	_	_	_	_	_
1200	_	_	_	_	_	_	_	_
1050-1150	_	_	_	_	_	C---O	C---O	_
690 and750	_	_	_	_	_	_	_	_

Appendix C

Scanning electron microscope (SEM)

PRINCIPLE OF SCANNING ELECTRON MICROSCOPE

The specimen is bombarded by a convergent electron beam, which is scanned across the surface. The electron beam generates a number of different types of signals, which are emitted from the area of the specimen where electron beam is impinging.

The induced signals are detected and the intensity of one of the signals (at a time) is amplified and used to modulate the inside of a cathode ray tube (CRT).Scanned synchronously with beam scanned across the specimen.

The electrons emitted from the electron gun are are focused on the object surface by means of a *Wehnelt* cylinder and two to three electromagnetic lenses; the diameter of the focal spot("diameter of the electron probe")which can at present be attained lies between five and ten nanometers.

A scan generator is controlled so that the electron beam scans the sample line-by-line, synchronized with the electron beam in the CRT monitor.

DESIGN

The secondary electrons (SE) and or backscattered electrons (BE) emitted from the samples can be measured. The signals emerging from the detectors serve to modulate the intensity on the screen.

Operating Modes

The SEM can be operated in many different modes where each mode is based on a specific type signal. The choice of operating mode depends upon the properties of the samples and on what features one wants to investigate. The more common modes are:

a. Secondary electrons

b. Backscattered electrons

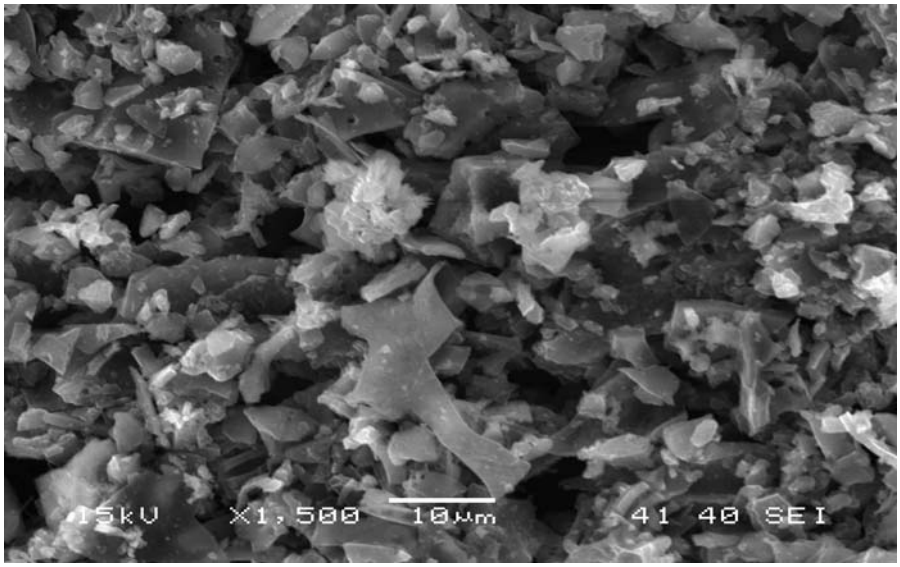
c. X-rays

a. Electrons with energies between 0-30 eV are detected and used to form the image. These electrons come from a layer within 5nm of the surface.

b. Elastically scattered electrons with energies ranging from few keV to the energy of the incident electrons (typically 15-30 keV) are detected .such electrons come From a volume extending down to .5m below the surface and therefore give information also about the "bulk" properties of the materials.

c. A material irradiated with high-energy electrons will emit X-rays: both as characteristic radiation and as continuous spectrum. The characteristic X-rays are, as the name implies , characteristic of the emitting element and can therefore be used to perform a compositional analysis of the specimen.

SEM of virgin adsorbents



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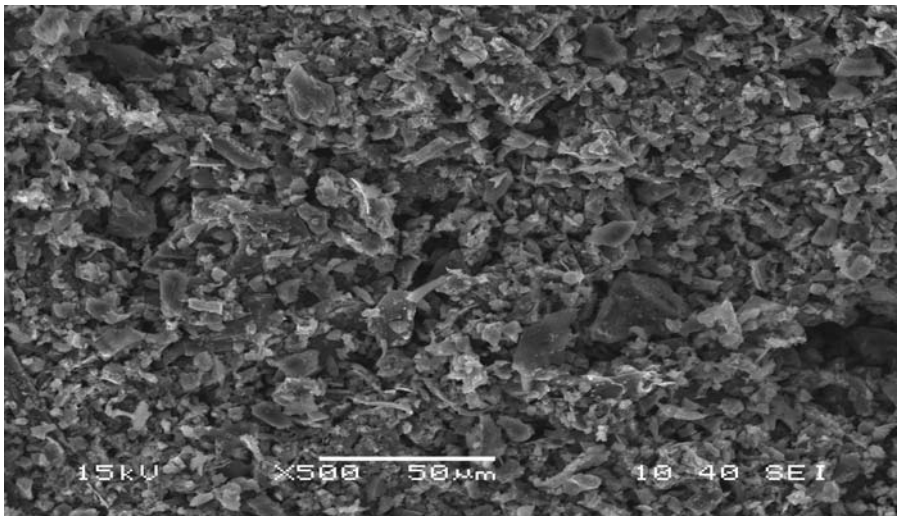

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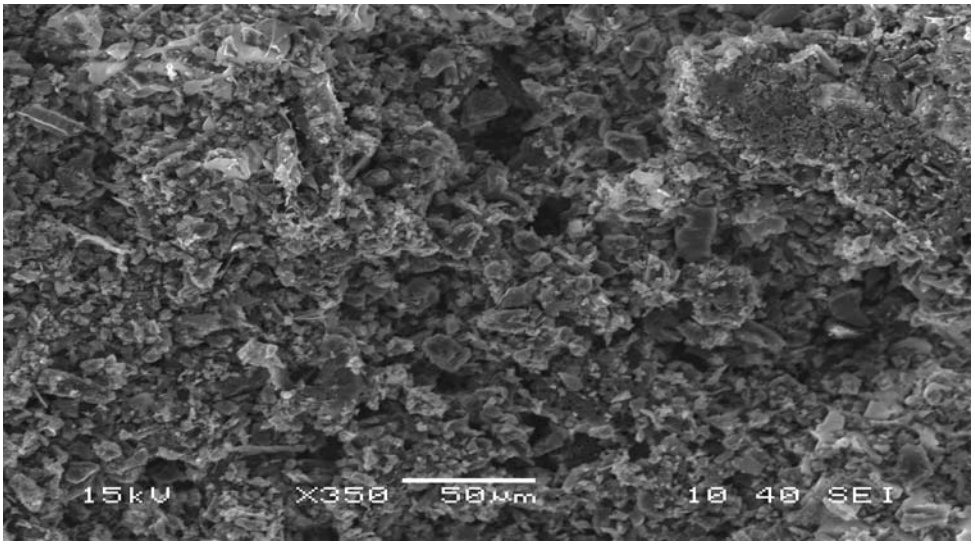
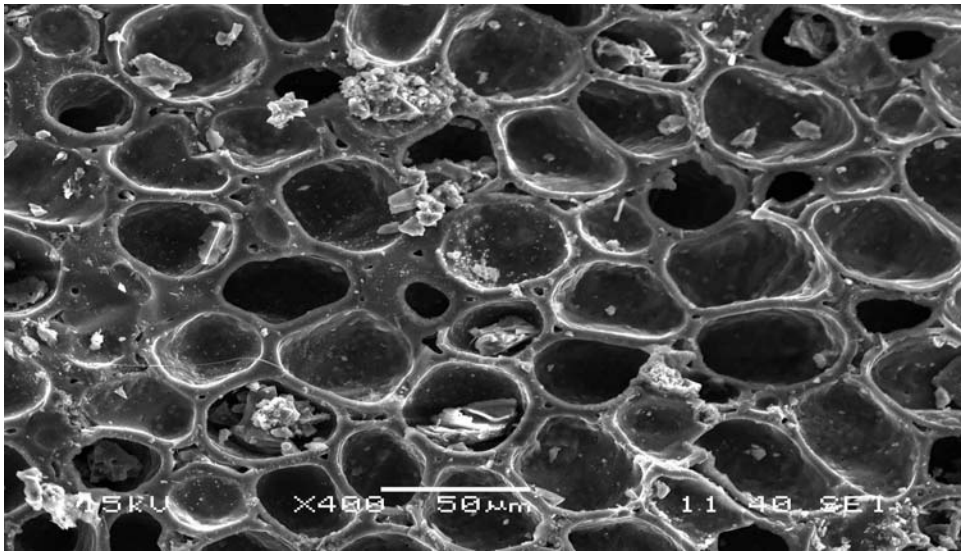


RHA



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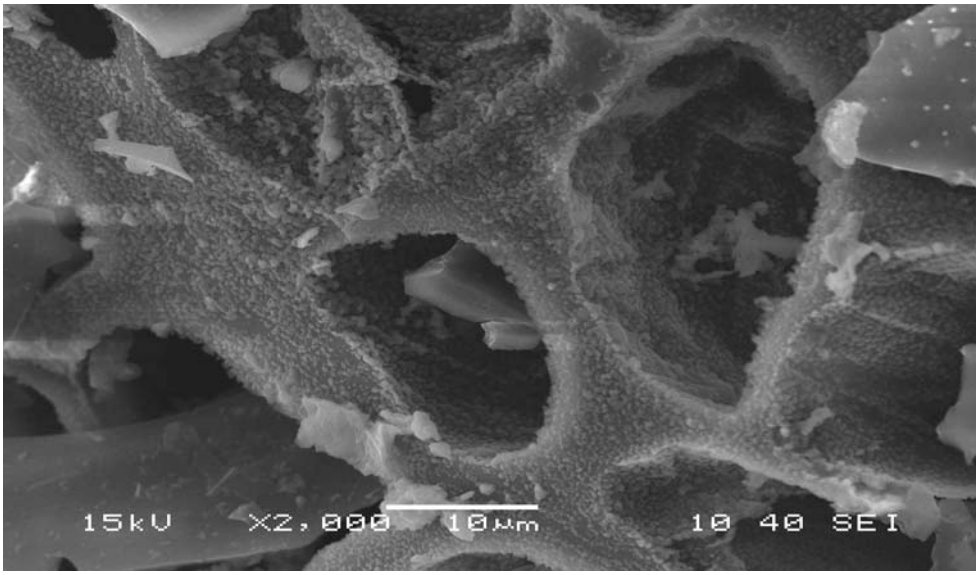

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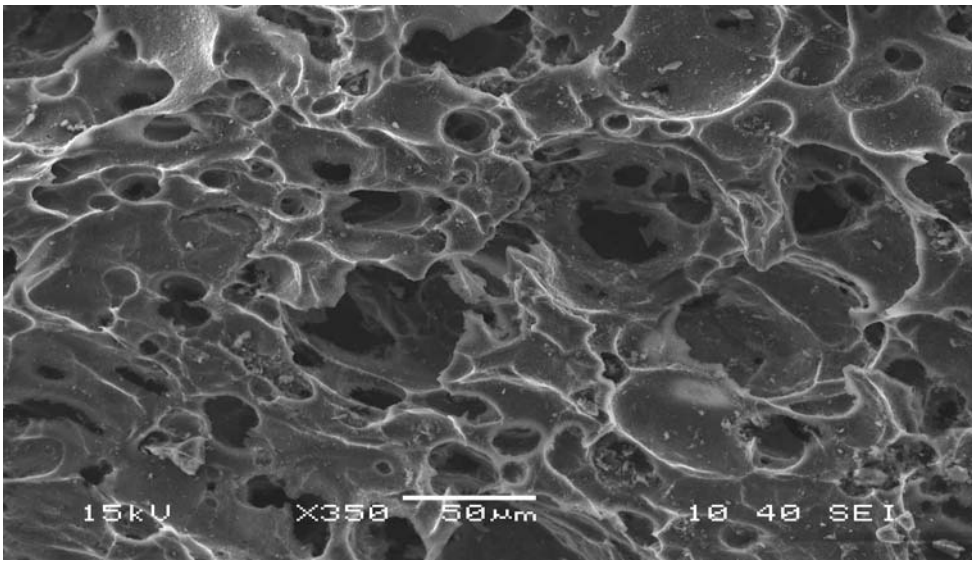
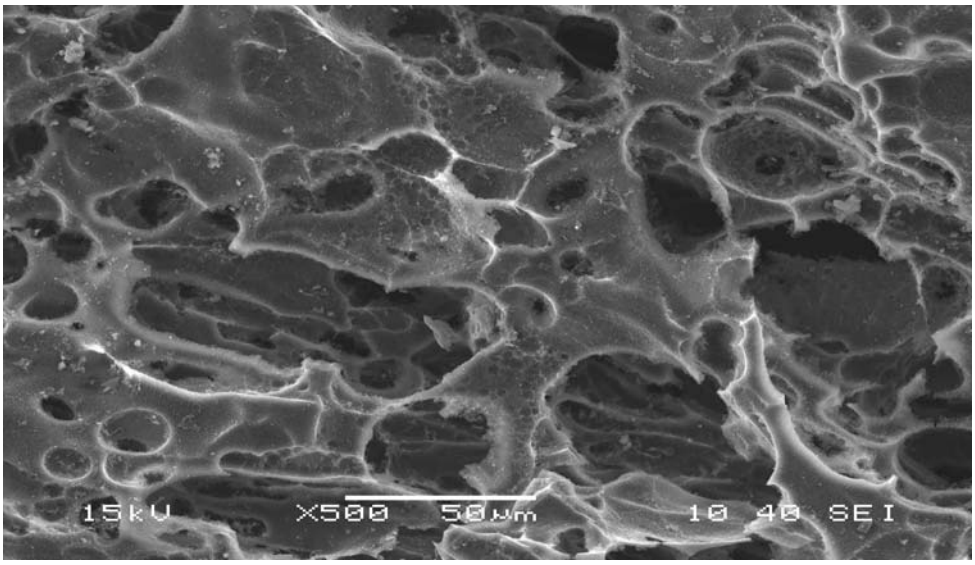
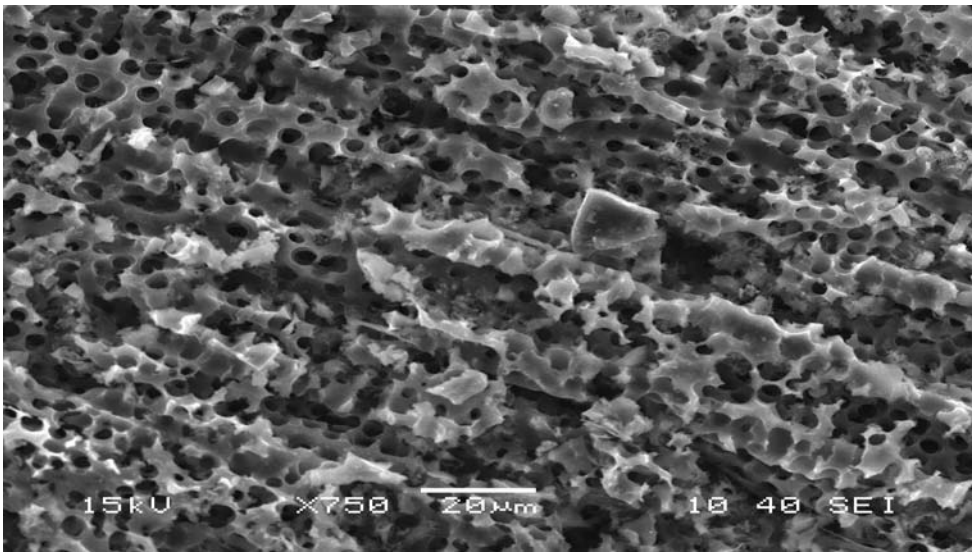


PAC

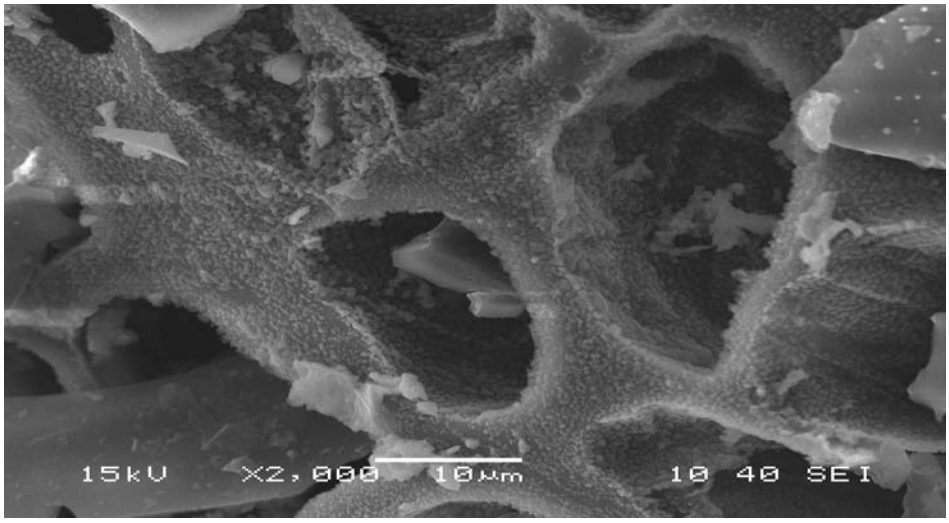


CCA



ST

SEM of CR loaded Adsorbents



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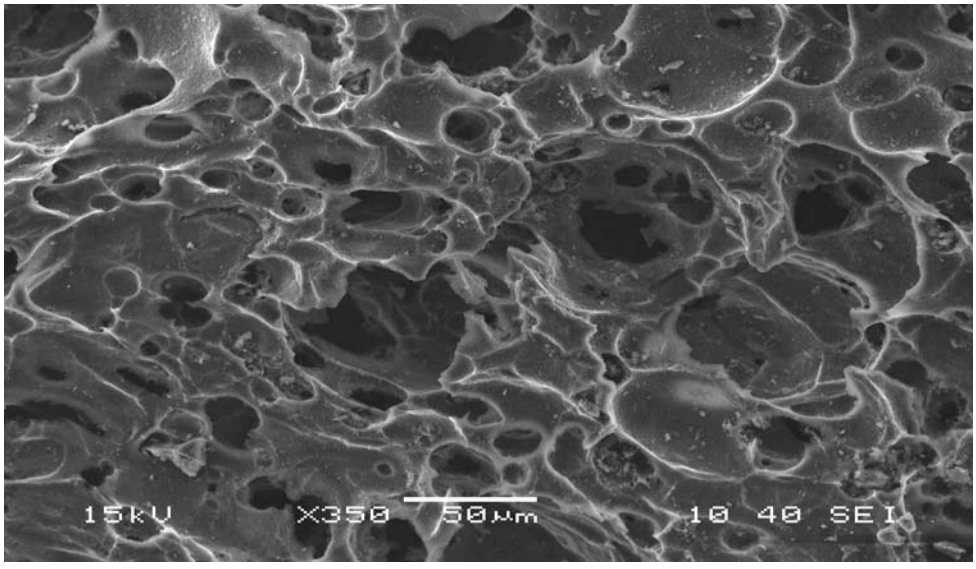
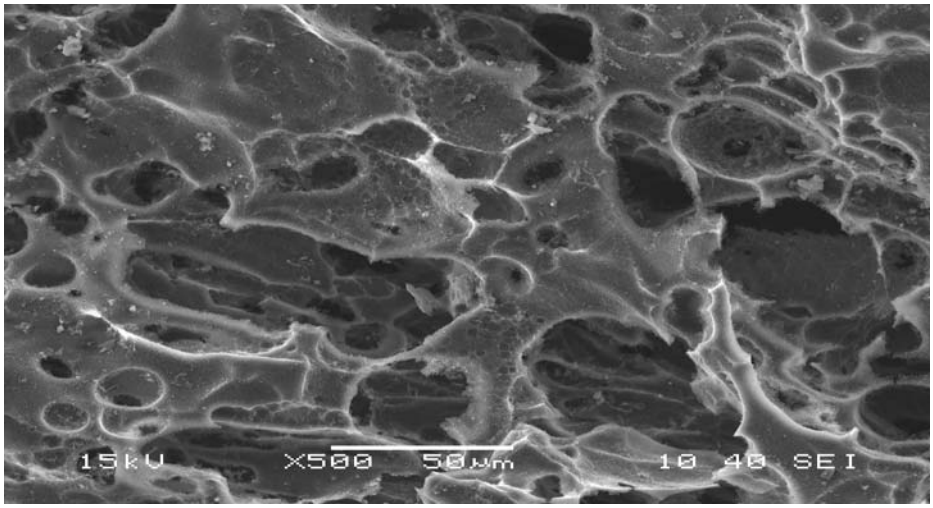
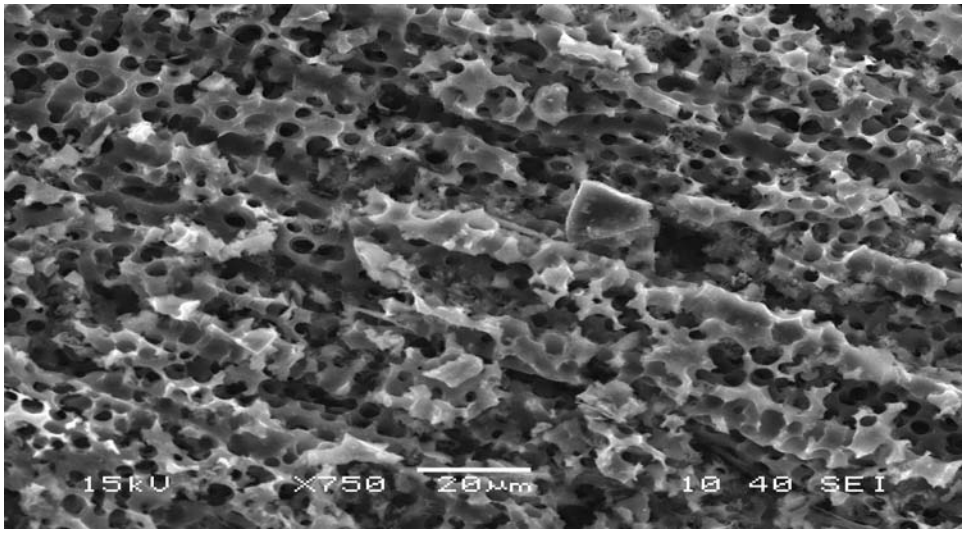


BAEL



RHA



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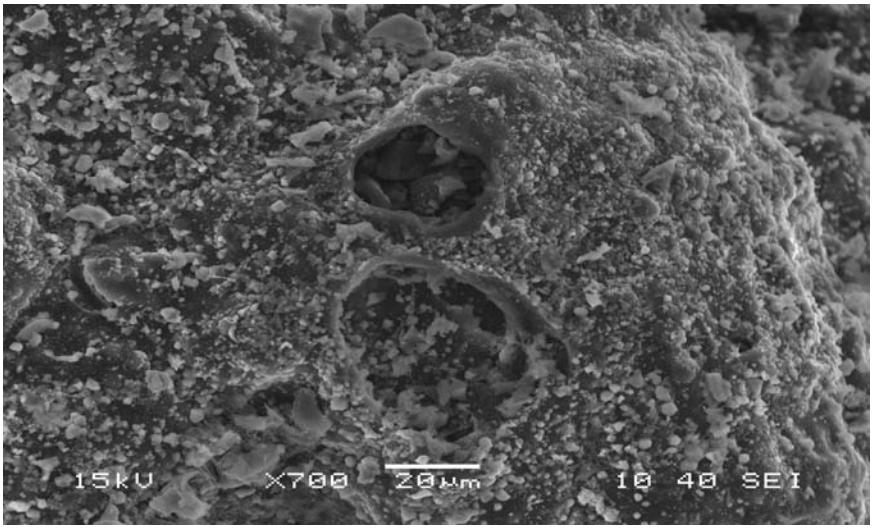

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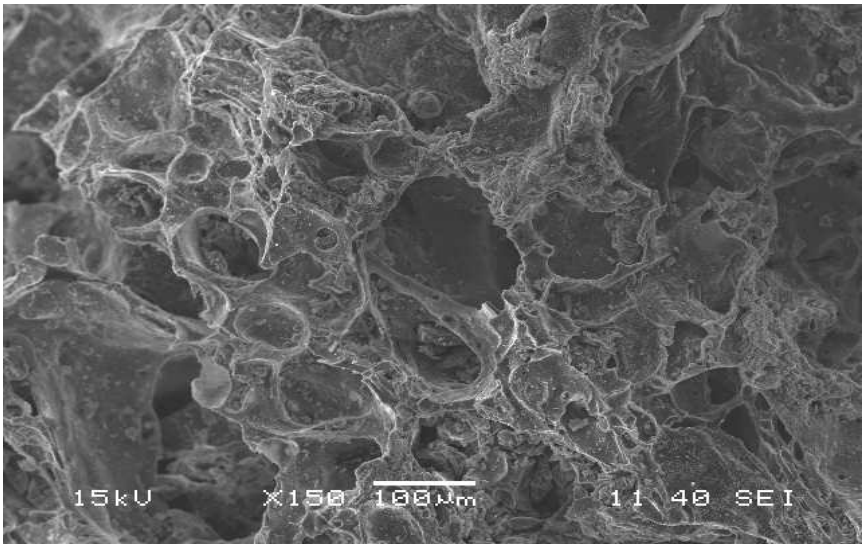

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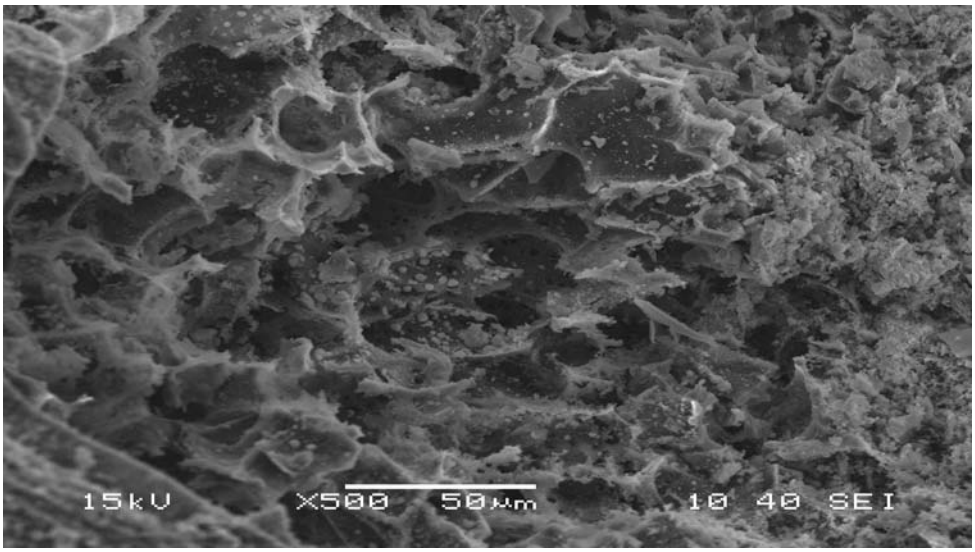

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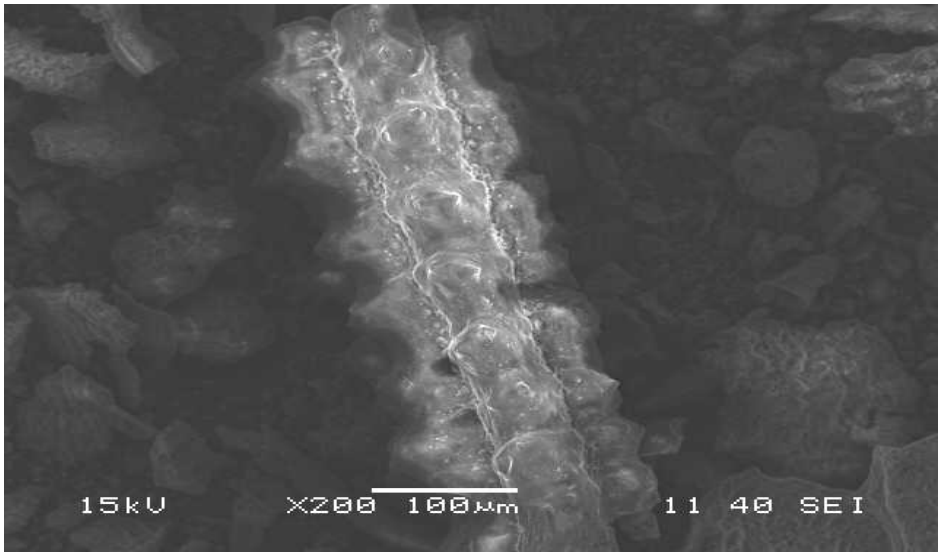

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